

# 17O-Excess Measurements of Water Without Fluorination Using Optical Spectroscopy

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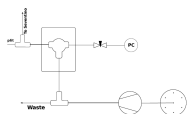
## Background

H<sub>2</sub><sup>17</sup>O is the third most abundant isotope of water, making up about 1 in every 2600 molecules of sea water. Meijer and Li performed electrolysis of water to generate O<sub>2</sub> from natural waters in 1998 and concluded <sup>17</sup>O fractionation is completely analogous to that of <sup>18</sup>O [1]. Barkan and Luz performed a similar measurement using CoF<sub>3</sub> treatment of H<sub>2</sub>O to generate in 2005 [2]. Based on their measured fractionation factor λ they proposed the definition of <sup>17</sup>O excess as:

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

## Experimental

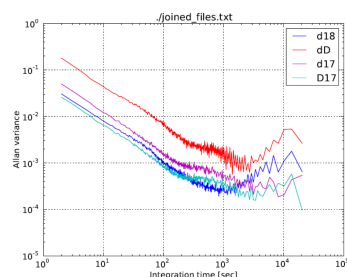
Recent advances in instrumentation allow the measurement of H<sub>2</sub><sup>17</sup>O directly as a water molecule. By coupling CRDS optical isotope measurements [3] with a continuous vaporization device shown below [4] it should be possible to measure <sup>17</sup>O excess directly from ice cores. This offers a more precise means to isolate the influence of diffusive processes since <sup>17</sup>O excess is only very weakly influenced by temperature-dependent equilibrium processes.



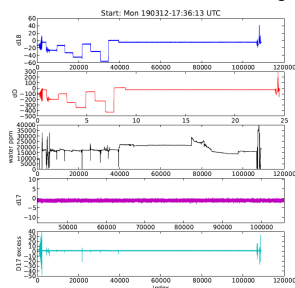
The analyzer used in this study was based on a commercial design from Picarro. The addition of extra optical components enabled measurements of absorption peaks unique to H<sub>2</sub><sup>17</sup>O in the region around 1400 nm. Rapid scanning and switching of optical regions was used to measure the concentrations of H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>18</sup>O, H<sub>2</sub><sup>17</sup>O, HD<sup>16</sup>O and by calculation their isotopes ratios and <sup>17</sup>O excess.

## Continuous Measurements

To quantify analytical precision and stability a continuous water vapor of constant isotopic composition and concentration for several hours. The variation in the signal of the individual isotope ratios and <sup>17</sup>O excess is shown in Figure 2 below.

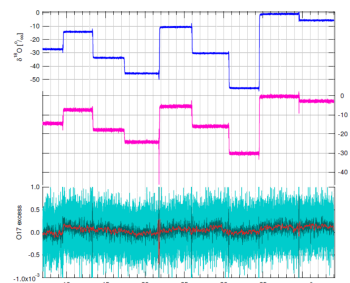


Different meteoric waters including depleted working standards were run in this fashion over the course of several hours. The signals for δ<sup>18</sup>O, δ<sup>17</sup>O, water concentration and <sup>17</sup>O excess are shown in Figure 3 below.

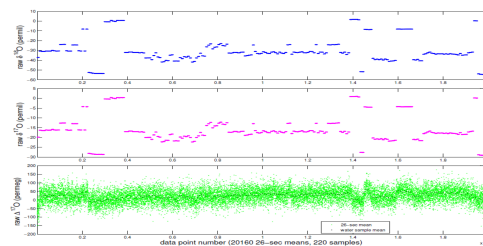


## Sample Analysis

A range of meteoric waters were run in this fashion over the course of several hours. The signals for δ<sup>18</sup>O, δ<sup>17</sup>O and <sup>17</sup>O excess are shown in Figure 4 below.

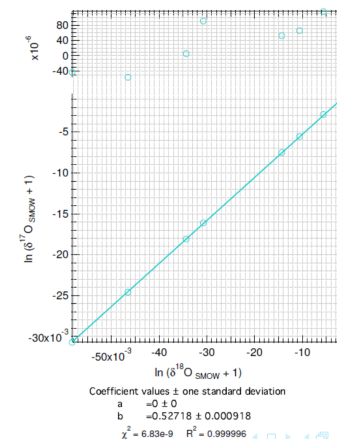


The signals for <sup>17</sup>O excess were quite small as expected. In terrestrial samples reported values of <sup>17</sup>O excess are below 40 per meg. A handful of IRMS laboratories worldwide perform <sup>17</sup>O excess measurements with the application required precision of 5 per meg, an example of such a measurement is shown in Figure 5 below.



## Fractionation Factor λ

By plotting the relationship of δ<sup>18</sup>O and δ<sup>17</sup>O and <sup>17</sup>O over a range of meteoric waters we measured λ to be 0.52718, this is the first known measurement of λ performed using optical isotope analysis.



## Conclusions and Future Work

<sup>17</sup>O excess of natural waters were rapidly measured using CRDS with a λ value in agreement with all previous studies. The simplicity of this measurement could radically transform measurements of <sup>17</sup>O excess. However standards for such measurements must still be agreed upon internationally.

1. Meijer and Li, Isotopes in Environmental Health Studies 34:4, 349-369 (1998)
2. Barkan and Luz, Rapid Comm. Mass. Spec. 19, 3737-3742 (2005)
3. Crosson et al, Appl. Phys. B Laser Optics 92, 403-408 (2008)
4. Gkinis et al, Atmos. Measur. Tech. Disc. 4, 4073-4101 (2011)