High resolution water stable isotopes continuous measurements

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1. Introduction
As fractionation of stable isotopes of water (H$_2^{16}$O, H$_2^{18}$O, HD$^{16}$O) occurs during the phase changes of water, their relative concentrations can be used as a "paleothermometer" in the interpretation of ice core records ¹, ². Ice-core drilling projects in Greenland and Antarctica have demonstrated the value of polar ice-cores as sensitive archives of the climatic variability.

Recently developed continuous flow analysis techniques permit the efficient use of ice-cores samples with high resolution. We present here a technique to realize high resolution continuous isotopic analysis of δ$^{18}$O and δD, on a liquid sample stream generated by a continuously melting ice core.

2. Method
The system is based on the work of Gkinis and colleagues ³, ⁴, and allows the continuous injection of very low water vapor sample flow to a Wavelength Scanned Cavity Ring Down Spectrometer (L2130-i, Picarro, Inc.). Regarding to its nominal gas flow rate, the WR-CRDS optimum performances are obtained by the continuous injection of sub μl/min water vapor flow. Such a very low vapor flow rate is achieved by the following method.

After being pumped through a 10μm stainless steel frit filter, the liquid sample flow goes in a stainless micro-volume Tee. It is then split between a 15cm long fused silica capillary leading to a homemade oven, and an overflow tube, with smaller inner diameter. This last tube generates a back-pressure, causing the sub μl/min flow rate through the capillary.

The fine mastery of this back-pressure, that controls the water level in the optical cavity, has been improved at two points. Firstly, the overflow tube is now divided into two sub-lines via a PEEK Tee. Secondly, one sub-line is controlled by adding a 10 turns needle valve ⁵.

The homemade oven heated to 180 ºC allows an instantaneously vaporization with 100% efficiency by mixing the water stream and dry air in a stainless steel Tee. The stream is then sent to the WR-CRDS inlet through a 6cm long 1/16" stainless steel tube maintained at 90 ºC to avoid any re-condensation and thus fractionation of the sample.

3. Results
We will present the system's stability, and its sensitivity on different vapor sample levels in the optical cavity.

We will show how we calibrate the spectrometer's measurements on a VSMOW scale, using standards with different isotopic compositions and also evaluate its memory effect performances.