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Improving accuracy and precision of water isotope measurements using Cavity Ring Down Spectroscopy

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Accurate stable isotopic measurements lie at the foundation of isotope geochemistry. Up until a decade ago isotopic measurements of water relied solely on isotope ratio mass spectrometers (IRMS). Recently, an alternative technology has been developed: Cavity Ring Down Spectroscopy (CRDS). The working principle behind it relies on the fact that water vapor is a greenhouse gas, which absorbs infra-red radiation. Instead of looking at different masses, a CRDS system differentiates the isotopologues of water vapor by their slightly different absorption wavelengths within the near infra-red spectra and quantifies their decay time. This development has allowed measurements of triple oxygen and hydrogen isotopes in both liquid water and vapor without the need to extract it from the air while achieving similar, or arguably better precision than conventional IRMSs. Despite their numerous advantages their accuracy is reduced due to a sample-to-sample carryover, known as the memory effect. Most of the literature today deals with this method by data correction algorithms.

In this presentation, we will demonstrate the working principle and potential behind this new technology and present a characterization of the memory effect and the accuracy problems it creates. The presentation will focus on a new method that we have developed that physically removes the memory effect by flushing the system with extremely depleted water vapor. This method, which is simple, not time consuming and is readily available, results in systematic improvement of instrumental accuracy. Validation of our method was done by constructing a normalized calibration curve and testing it against international standards. We further tested this method using standards of a wide range of isotopic compositions and derived a generalized method for its application. The results show that our method can be used to easily and routinely measure all 4 main isotopologues of liquid water and vapor at higher accuracy and reproducibility than are presently described in the literature.