

Why ^{17}O -excess? (And, what is it?)

Advances in cavity ring-down spectroscopy (CRDS) have enabled scientists around the world to make quick, easy and highly precise measurements of the stable isotopes of oxygen and hydrogen in water – in the field and in the lab. To date, the focus has been on the two most common isotope measurements in water: $\delta^{18}\text{O}$ and δD , with applications to paleoclimate, hydrology, and biogeochemistry.

But, if we broaden our scope we can accomplish much more. Although most studies focus on the abundance of the heaviest stable isotope of oxygen, ^{18}O , relative to the more prevalent, light isotope, ^{16}O , there is another stable isotope of oxygen, ^{17}O , which often goes overlooked. ^{17}O comprises less than 0.04% of all naturally-occurring stable oxygen. It can be used to learn more about **past humidity** (from ice cores), **evapotranspiration** (from leaf and stem water), and the **general evaporative regime** (from liquid water), among other things. There are challenges though – first and foremost, due to its **small signal variability**, measuring ^{17}O requires instrumentation capable of **extremely high precision** (better than 0.01 ‰, or 10 per meg). Second, traditional techniques used to measure ^{17}O require conversion to O_2 – a complicated and time-consuming methodology, which can only be done in a lab.

In almost all natural processes, the preference for one isotope over another is related to the mass of each isotope – commonly referred to as “mass-dependent fractionation”. For oxygen, this means that the preference for ^{18}O relative to ^{16}O (2 atomic mass units difference) is approximately twice as much as the preference for ^{17}O over ^{16}O (1 atomic mass unit difference). For example, consider the fractionation of oxygen isotopes during a rainfall event: due to the stability of bonds in an H_2O molecule, ^{18}O preferentially goes into the liquid phase leaving the remaining water vapor depleted in heavy isotopes. In terms of delta notation, the remaining water vapor has a smaller $\delta^{18}\text{O}$ and δD than it had initially. Conversely, the rainfall itself is enriched in ^{18}O , i.e., it has a larger $\delta^{18}\text{O}$ and δD than the cloud from which it precipitated. If we assess the same event in terms of $\delta^{17}\text{O}$, the *preference for ^{17}O in the liquid phase is approximately half as much as the preference for ^{18}O* . As a result, $\delta^{17}\text{O}$ of the remaining water and the rainfall will be approximately half of $\delta^{18}\text{O}$. This can be visualized by plotting $\delta^{18}\text{O}$ versus $\delta^{17}\text{O}$ (“a triple isotope plot”) which will yield a line of data points with a slope of approximately 0.5 (figures 1 and 2).

With a few exceptions, almost all terrestrial materials fall on this line. However, closer inspection reveals that the slope is not exactly 0.5, but slightly larger, and that different processes induce slightly different slopes. In particular, almost all meteoric waters, from the tropics to the ice of the Polar Regions, yield a slope of 0.528 (Meijer and Li, 1998). This slope is the manifestation of the combined effects of equilibrium fractionation between the liquid and vapor phases (with a slope of 0.529; Barkan and Luz, 2005) and

kinetic processes, such as evaporation, condensation, vapor diffusion through air, and leaf transpiration, all of which are associated with shallower slopes (< 0.52).

To assess the anomaly from an expected relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, scientists have defined the parameter $\Delta^{17}\text{O}$:¹

$$\Delta^{17}\text{O} \approx \delta^{17}\text{O} - \lambda\delta^{18}\text{O}$$

For the specific case of water, $\Delta^{17}\text{O}$ is known as “ ^{17}O -excess”, and it quantifies the deviation from the “Global Meteoric Water Line”, where $\lambda = 0.528$. This excess in ^{17}O can be used to probe the hydrological system, adding additional information over the more traditional “deuterium-excess” (d-excess = $\delta\text{D} - 8\delta^{18}\text{O}$) because **^{17}O -excess is much less sensitive to changes in temperature.** Uemura et al. (2010) measured ^{17}O -excess in marine water vapor and found a negative correlation with relative humidity, while ^{17}O -excess records from polar ice cores provide valuable information of past changes in the global hydrological cycle, e.g., large scale variations in relative humidity over the ocean or the moisture origin of precipitation sites (Landais et al., 2008; Winkler et al., 2012). Measurements of ^{17}O -excess in leaf waters have also been used to probe global productivity which links atmospheric oxygen and the water cycle via photosynthesis and respiration (Landais et al., 2006). In each of these cases, the magnitude of ^{17}O -excess tends to be very small (10s of per meg, or less than 0.01 ‰), and therefore, extremely high precision measurements are required (typically 5-8 per meg).

Using **traditional** isotope ratio mass spectrometry, it is **not possible to measure ^{17}O -excess directly from water** or via conversion to CO_2 (often used for measuring $\delta^{18}\text{O}$ in water) due to isobaric interferences. Therefore, researchers have to convert H_2O to O_2 using fluorination chemistry, and then analyze the resultant O_2 for several hours to get the required precision from isotope ratio mass spectrometry. This is a complex process with a variety of safety concerns, resulting in only a handful of labs around the world measuring ^{17}O -excess.

To make meaningful measurements of anomalies in ^{17}O , high precision measurements of both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are required. It is simply not good enough to determine $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ with a precision of 0.03‰ – the science dictates better than this. Interested in learning more? Please contact Kate Dennis, Product Manager of Isotopic Water at Picarro (kdennis@picarro.com).

¹ The strict definition of $\Delta^{17}\text{O}$ utilizes log notation, omits the factor of 1000 in delta notation, and allows the user to specify the slope, λ :

$$\Delta^{17}\text{O} = \ln(\delta^{17}\text{O} + 1) - \lambda \ln(\delta^{18}\text{O} + 1)$$

References:

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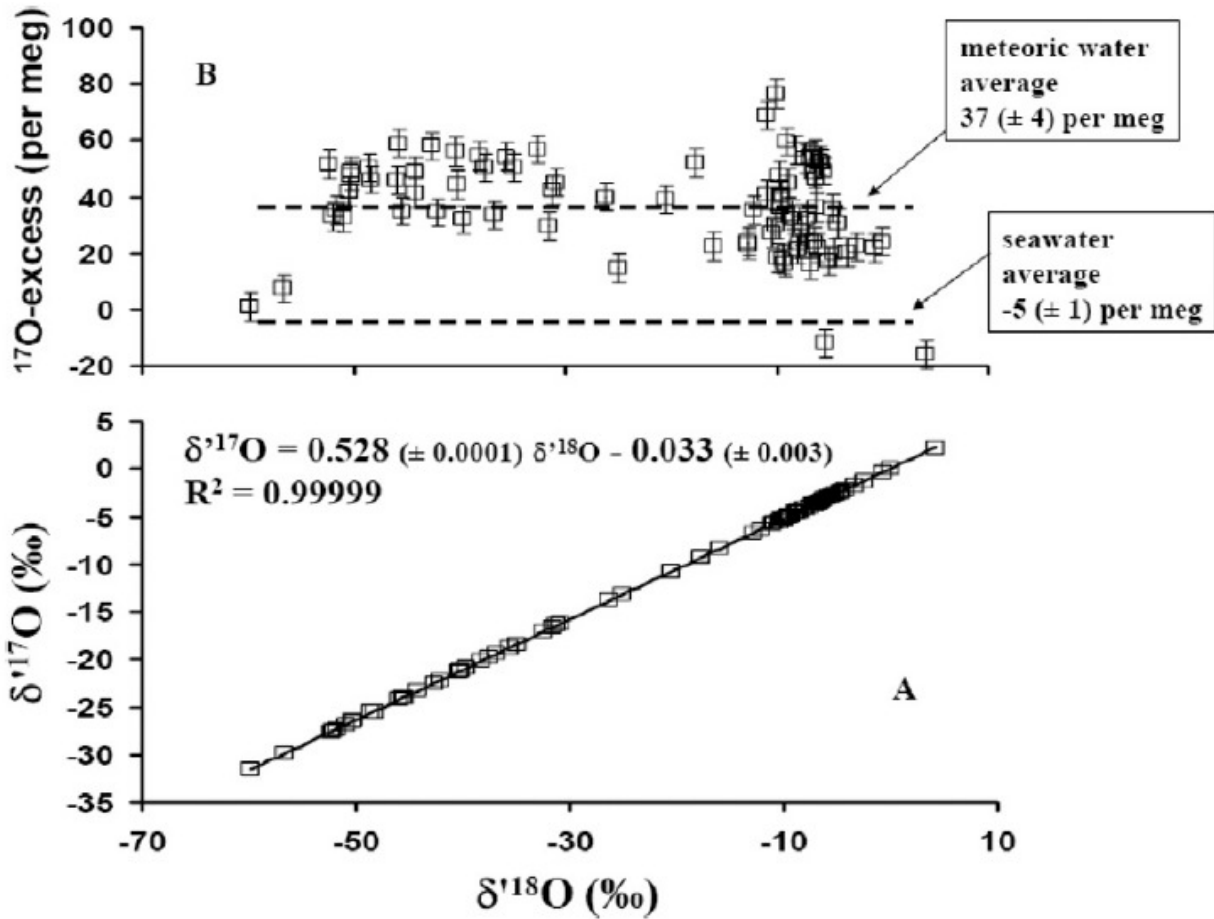


Figure 1: The relationship for meteoric waters is visualized in plots of $\delta^{18}\text{O}$ versus $\delta^{17}\text{O}^2$, and $\delta^{18}\text{O}$ versus $^{17}\text{O}\text{-excess}$ (figure from Luz and Barkan, 2010; data from Barkan and Luz, 2005; Luz and Barkan, 2010; Landais et al., 2008). Here the authors plot data for both meteoric waters and seawater, and demonstrate that meteoric water has an excess of ^{17}O isotopes relative to that of oceanic water.

² $\delta^{i17}\text{O} = \ln(\delta^{i17} + 1) = \ln\left(\frac{1.173496}{1.17349}\right)$

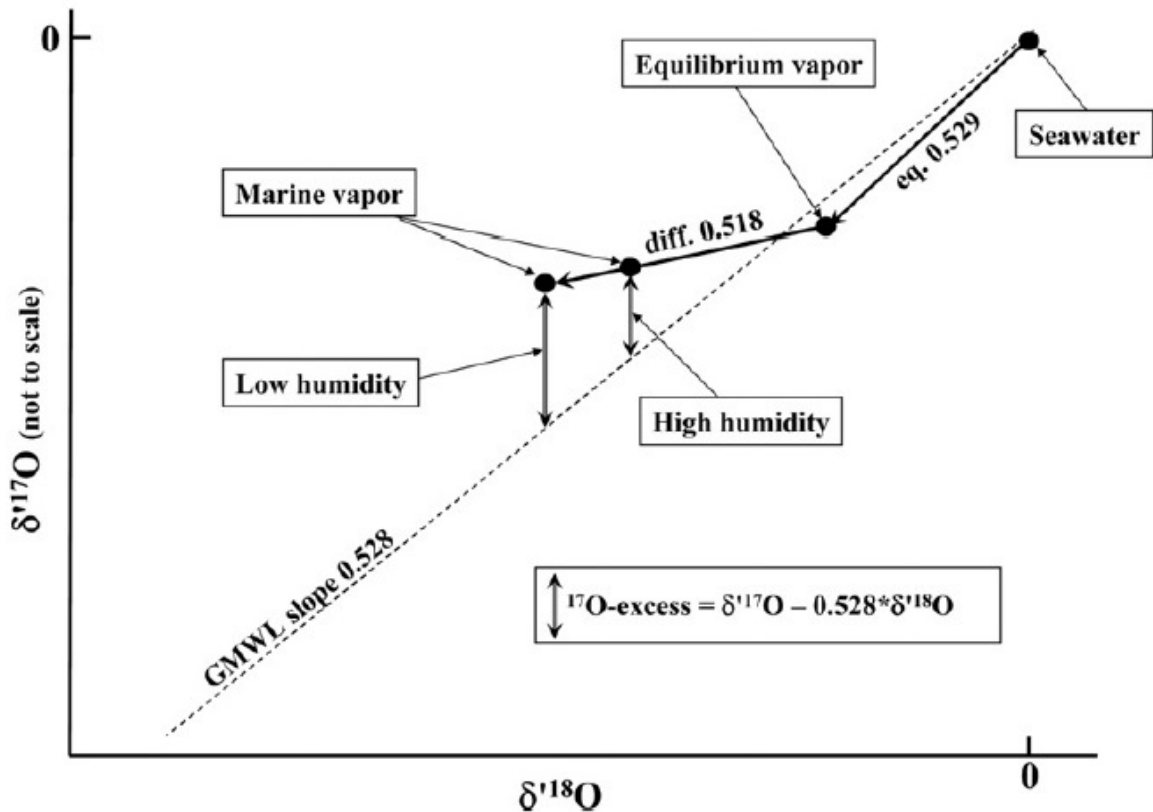


Figure 2: To help visualize how an excess in ^{17}O manifests itself, vector diagrams of processes with different slopes are helpful. In this example, from Luz and Barkan (2010), the origin of ^{17}O -excess for marine water vapor is shown. Water vapor formed in the immediate vicinity above the ocean (100% humidity) will follow equilibrium fractionation with a slope of 0.529, resulting in a slight depletion in ^{17}O relative to the GMWL. Now upon diffusing into dry air, the slope decreases to ~ 0.518 . This results in a ^{17}O -excess in the water vapor, which will evolve dependent on the relative humidity of the air parcel.