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## Triple isotope composition of oxygen in atmospheric water vapor

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[1] Recently, an excess of  $^{17}\text{O}$  ( $^{17}\text{O}$ -excess) has been demonstrated in meteoric water and ice cores. Based on theory and experiments, it has been suggested that this excess originates from evaporation of ocean water into under-saturated air. However, there has never been direct demonstration of this excess in marine vapor. Here, we present results of the first measurements of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  in vapor samples collected over the South Indian and the Southern Oceans. Our data show the existence of  $^{17}\text{O}$ -excess in marine vapor and also clear negative correlation between  $^{17}\text{O}$ -excess and relative humidity. Thus,  $^{17}\text{O}$ -excess is useful for constraining oceanic humidity in hydrological and climatic models. Using the obtained values of  $^{17}\text{O}$ -excess, we estimated the fractionation factor between  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{16}\text{O}$  for diffusion in air above the ocean ( $^{18}\alpha_{\text{diff}}$ ). The new estimation of  $^{18}\alpha_{\text{diff}}$  (1.008) is larger than the widely accepted value in hydrological studies. **Citation:** Uemura, R., E. Barkan, O. Abe, and B. Luz (2010), Triple isotope composition of oxygen in atmospheric water vapor, *Geophys. Res. Lett.*, 37, L04402, doi:10.1029/2009GL041960.

### 1. Introduction

[2] Stable isotopes of water are widely used as hydrological or climatological tracers [Gat, 1996]. While  $^{17}\text{O}/^{16}\text{O}$  ( $\delta^{17}\text{O}$ ) in water has been assumed to carry no additional information, an excess of  $\delta^{17}\text{O}$  in meteoric water is expected if evaporation from the ocean is out of equilibrium between vapor and liquid [Angert *et al.*, 2004].

[3] Recently, triple isotope composition of oxygen ( $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$ ) have been measured in meteoric waters from different climate regions [Meijer and Li, 1998; Landais *et al.*, 2006; Landais *et al.*, 2008]. When the results are displayed in a  $\ln(\delta^{17}\text{O} + 1)$  vs.  $\ln(\delta^{18}\text{O} + 1)$  plot, all the samples fall above a line with a slope of 0.528 with an significant intercept. Barkan and Luz [2007] defined the  $^{17}\text{O}$ -excess as:

$$^{17}\text{O}\text{-excess} = \delta'^{17}\text{O} - 0.528 \cdot \delta'^{18}\text{O}, \quad (1)$$

where  $\delta'$  is a modified delta notation [Hulston and Thode, 1965],  $\delta'^*\text{O} = \ln(\delta^*\text{O} + 1)$ ; and "\*" stands for 17 or 18. Because the magnitudes of the  $^{17}\text{O}$ -excess are very small, they are multiplied by  $10^6$  and are reported in "per meg"

with respect to VSMOW. Barkan and Luz [2007] demonstrated that the relationship between the isotope fractionations in vapor-liquid equilibrium and vapor diffusion in air is different and suggested how this would give rise to  $^{17}\text{O}$ -excess in marine vapor and meteoric water. However,  $^{17}\text{O}$ -excess has never been demonstrated in marine vapor.

[4] Marine water vapor is very suitable for investigation of evaporation mechanisms over the ocean because it is far less affected by subsequent precipitation and snow formation processes. In a recent paper, Uemura *et al.* [2008] studied the effects of evaporation on  $\delta^{18}\text{O}$  and  $\delta\text{D}$  on vapor sampled over the open sea. Here we use the same sample set to investigate  $^{17}\text{O}$ -excess, and how conditions near the ocean surface (humidity, temperature, and wind-speed) control it.

### 2. Sampling and Isotopic Measurements

[5] Water vapor was collected cryogenically on board ship over the South Indian and the Southern Oceans. The details on sampling locations and methods are given by Uemura *et al.* [2008]. Briefly, the vapor sampling and relative humidity measurements were conducted at ~15m above the sea surface. There are no reliable wind speed measurements at this height and instead we used hourly measurements at the mast (~30m above the sea surface).

[6] The  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  measurements of water have been conducted at the Hebrew University of Jerusalem using a water fluorination method [Barkan and Luz, 2005]. We measured 53 samples. The analytical errors (standard error of the mean ( $n = 90$ ) multiplied by Student's t-factor for a 95% confidence limits) in  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  are 0.004 and 0.008%, respectively. The reproducibility of  $^{17}\text{O}$ -excess is 5 per meg. The measurements were run against a working  $\text{O}_2$  standard calibrated against VSMOW.

### 3. Results

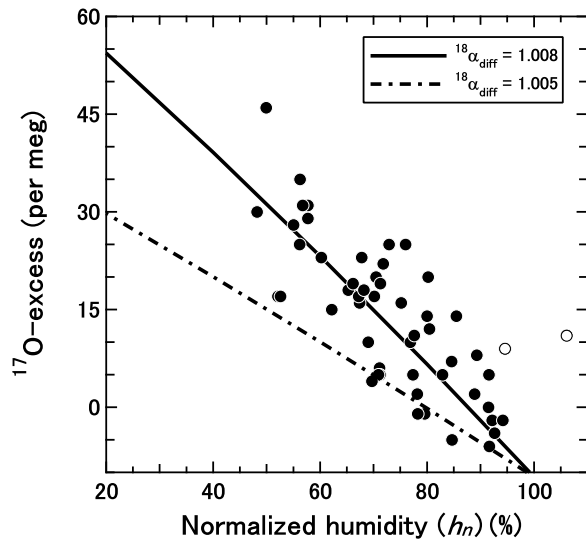
[7] All the data are given in Table S1 of the auxiliary material.<sup>4</sup> We note, that the present  $\delta^{18}\text{O}$  values are systematically higher (~0.8‰ in average) than those of Uemura *et al.* [2008]. This enrichment is most probably due to the long-term (~2 year) storage and small evaporative loss. However, the difference in  $\delta^{18}\text{O}$  does not correlate with the  $^{17}\text{O}$ -excess values ( $R^2 = 0.05$ ), suggesting that the storage in bottles does not affect the  $^{17}\text{O}$ -excess values.

[8] In Figure 1, we show the  $^{17}\text{O}$ -excess vs. normalized relative humidity (hereafter  $h_n$ ).  $h_n$  is defined as water vapor concentration in the air divided by the saturated vapor concentration at ocean surface temperature. As can be seen,  $^{17}\text{O}$ -excess is slightly negative at high  $h_n$  and increases as the humidity goes to low values. A linear regression yielded

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**Figure 1.** The  $^{17}\text{O}$ -excess of atmospheric vapor in the ocean versus normalized humidity ( $h_n$ ). Observed data (solid circles) with two outliers (open circles) are shown. The solid line is based on model calculations with optimized  $^{18}\alpha_{\text{diff}}$  (1.008). The chain line is based on model calculations with the generally accepted  $^{18}\alpha_{\text{diff}}$  values of 1.005.

a slope of  $-0.64$  (per meg/%), with a statistically significant correlation coefficient ( $R^2 = 0.56$ ,  $P < 0.001$ ,  $n = 53$ ).

[9] A positive correlation between  $^{17}\text{O}$ -excess and sea surface temperature (SST) was observed with the slope of the linear regression of  $1.2$  per meg/ $^{\circ}\text{C}$ . The SST also correlates with d-excess ( $=\delta\text{D} - 8 \delta^{18}\text{O}$ ) [Uemura et al., 2008]. In the latter case, this correlation can be explained by the fact that the magnitude of d-excess is also influenced by liquid-vapor equilibrium, which is temperature dependent. However, in contrast to d-excess, the major controlling factor for  $^{17}\text{O}$ -excess is relative humidity [Barkan and Luz, 2007]. The simple evaporation model shows insignificant impact of SST on  $^{17}\text{O}$ -excess ( $\sim 0.1$  per meg/ $^{\circ}\text{C}$ ). Therefore, the observed correlation of  $^{17}\text{O}$ -excess with SST is mainly the result of the covariance of the latter with relative humidity.

[10] Below we show that, to a large extent, the negative correlation between  $^{17}\text{O}$ -excess and relative humidity can be explained with a simple concept [Craig and Gordon, 1965], in which moisture above the ocean is assumed to be derived only from local evaporation. This, of course, is an over simplification and we will discuss possible complications arising from mixing of moisture from non local sources.

## 4. Discussion

### 4.1. Principles of the Evaporation Model

[11] Based on the Craig-Gordon model [Craig and Gordon, 1965] with the approach of Merlivat and Jouzel [1979], Barkan and Luz [2007] derived an equation which relates the  $^{17}\text{O}$ -excess to  $h_n$ ;

$$^{17}\text{O-excess} = -\ln\left\{^{18}\alpha_{\text{eq}}^{0.529}\left(^{18}\alpha_{\text{diff}}^{0.518}(1-h_n)+h_n\right)\right\} + 0.528\ln\left\{^{18}\alpha_{\text{eq}}\left(^{18}\alpha_{\text{diff}}(1-h_n)+h_n\right)\right\}. \quad (2)$$

The terms on the right correspond to  $\delta^{17}\text{O} - 0.528 \cdot \delta^{18}\text{O}$  in equation (1) for steady-state vapor above an ocean. For such steady-state case, these terms can be calculated from the fractionation factors for equilibrium ( $^{17}\alpha_{\text{eq}}$  and  $^{18}\alpha_{\text{eq}}$ ) and diffusion ( $^{17}\alpha_{\text{diff}}$  and  $^{18}\alpha_{\text{diff}}$ ). The exponent 0.529 relates the  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  fractionation factors for liquid-vapor equilibrium ( $^{17}\alpha_{\text{eq}} = ^{18}\alpha_{\text{eq}}^{0.529}$ ), which was experimentally determined by Barkan and Luz [2005]. Similarly, the exponent 0.518 relates the fractionation factors for vapor diffusion in air ( $^{17}\alpha_{\text{diff}} = ^{18}\alpha_{\text{diff}}^{0.518}$ ) [Barkan and Luz, 2007].

[12] For convenience, we defined the fractionation factors ( $\alpha$ ) such that they are greater than 1. In this case,  $^{18}\alpha_{\text{diff}} = 1.028$  means that  $\delta^{18}\text{O}$  differences between liquid and vapor is approximately 28%.  $\alpha_{\text{diff}}$  corresponds to  $1/(1-k)$  where  $k$  is a kinetic factor used by Merlivat and Jouzel [1979].

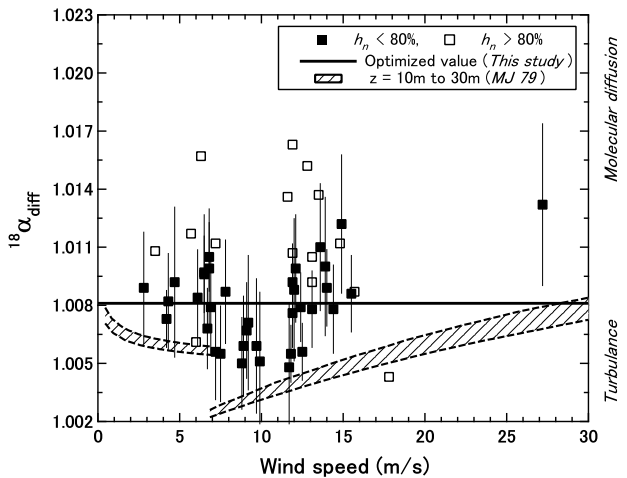
[13] The equilibrium fractionation factor,  $^{18}\alpha_{\text{eq}}$ , depends on temperature [e.g., Horita and Wesolowski, 1994] and thus varies considerably over the oceans. However, as shown by Barkan and Luz [2005] the ratio  $\ln(^{17}\alpha_{\text{eq}})/\ln(^{18}\alpha_{\text{eq}})$  equals 0.529 over the temperature range 11 to  $42^{\circ}\text{C}$ , and from theory [Van Hook, 1968] it is expected to remain the same over all the relevant temperatures observed in our study. Therefore,  $^{17}\text{O}$ -excess in equation (2) is not sensitive to temperature variations. In contrast,  $^{17}\text{O}$ -excess strongly depends on  $^{18}\alpha_{\text{diff}}$ . For example, Figure 1 shows lines calculated with equation (2) for two different values of  $^{18}\alpha_{\text{diff}}$  at temperature of  $10^{\circ}\text{C}$ .

### 4.2. Estimation of the Diffusion Factor

[14] The value of  $^{18}\alpha_{\text{diff}}$  ranges from 1.0 (pure turbulence) to 1.0028 (pure molecular diffusion [Merlivat, 1978; Barkan and Luz, 2007]). Theoretically, this value should depend on wind speed, which affects the strength of turbulence and aerodynamic conditions. Based on wind tunnel experiments, Merlivat and Jouzel [1979, hereafter MJ79] derived semi-empirical formula of wind-speed dependency of  $\alpha_{\text{diff}}$ , for both smooth and rough water surfaces. The most puzzling feature of MJ79 estimation is a discontinuity of  $^{18}\alpha_{\text{diff}}$  at wind-speed  $\sim 7\text{m/s}$ , where transition from smooth to rough regimes occurs (Figure 2). Although this formula has never been confirmed by observations from the open ocean, it has been widely used in the isotope modeling for the evaporation in the ocean. Because mid latitude regions of the oceans in southern hemisphere host the strongest wind fields at the ocean surface [Yuan, 2004], many of our data points correspond to the rough regime. Thus, this data set is very suitable for comparison with the MJ79 formula.

[15] We estimated  $^{18}\alpha_{\text{diff}}$  for each sample point by substituting values of  $^{18}\alpha_{\text{eq}}$  [Horita and Wesolowski, 1994] and  $^{17}\text{O}$ -excess obtained in the present study into equation (2). As shown in Figure 2, the calculated  $^{18}\alpha_{\text{diff}}$  values are scattered and there is no clear trend with respect to wind speed. In general, all our estimates are larger than those of MJ79 ( $\sim 1.005$ ). Two outliers (indicated in Figure 1 and Table S1) were rejected from the calculation. The reason for their large deviation from the general trend in Figure 1 is not clear. We note, however, that in both cases the samples were collected during storm, and probably these samples were contaminated due to the difficulty of handling them properly under such conditions.

[16] The optimal value of  $^{18}\alpha_{\text{diff}}$  representing our data was calculated by minimizing the root mean square error



**Figure 2.** Plot of  $^{18}\alpha_{\text{diff}}$  vs. wind speed. The  $^{18}\alpha_{\text{diff}}$  values were calculated with equation (2). The solid squares indicate the values for which  $h_n$  is smaller than 80%, and the solid line represents the average value of these points. The open squares are the values for which  $h_n$  is greater than 80%. For clarity, and because the calculation error is large, these points are shown without error bars (see text). The gray shaded area represents the  $^{18}\alpha_{\text{diff}}$  calculated with the formula of Merlivat and Jouzel [1979] for 10 m height (upper dashed line) and 30 m height (lower dashed line).

(RMSE) between calculated and observed points. The minimum RMSE (7.1 per meg) was found for  $^{18}\alpha_{\text{diff}}$  of  $1.0083 \pm 0.0018$ . With this  $^{18}\alpha_{\text{diff}}$ , the observed and modelled  $^{17}\text{O}$ -excess linearly correlate with a slope of 0.79 ( $R^2 = 0.65$ ,  $n = 51$ ).

[17] We also estimated the optimal values of  $^{18}\alpha_{\text{diff}}$  from individual data point shown in Figure 2. Taking into account errors in  $^{17}\text{O}$ -excess ( $\pm 5$  per meg) and relative humidity measurement ( $\pm 5\%$ ), the error in the  $^{18}\alpha_{\text{diff}}$  ranges from  $\pm 0.001$  to  $\pm 0.005$  for  $h_n$  smaller than 80%. For  $h_n$  greater than 80% the error in the calculation sharply increases (up to about  $\pm 0.04$ ). Then, excluding the points where  $h_n$  is greater than 80%, the average value is 1.0081. Some of the points used for deriving this value are below the temperature range over which Barkan and Luz [2005] calculated  $\ln(^{17}\alpha_{\text{eq}})/\ln(^{18}\alpha_{\text{eq}})$ . However, we note that removing these points results in  $^{18}\alpha_{\text{diff}}$  estimate of 1.0080 which is well in the error range of the 1.0081 estimate.

[18] Interestingly, after the rejection of data with large uncertainty, slight wind-dependency of  $^{18}\alpha_{\text{diff}}$  can be seen (Figure 2). The  $^{18}\alpha_{\text{diff}}$  values show broad minimum around wind speed between 8 to 11 m/s, which might correspond to the transition zone between smooth and rough regimes. For example, if we choose the transition between the two regimes at a wind speed of 7.8 m/s (Reynolds number  $\sim 1$ ), our data give statistically significant correlation for the rough regime ( $^{18}\alpha_{\text{diff}} = 0.000454 U + 1.002192$ ,  $R^2 = 0.54$ ). This formula improved the linear correlation between modelled and observed  $^{17}\text{O}$ -excess (RMSE = 6.2 per meg, slope = 0.85,  $R^2 = 0.74$ ,  $n = 51$ ). However, the improvement of correlation is marginal. In addition, the equation strongly depends on one point at high wind speed and the regression depends on arbitrary choice of a transition value of  $U$ . Thus,

we suggest that one value ( $^{18}\alpha_{\text{diff}} = 1.008$ ) should be used in modelling studies.

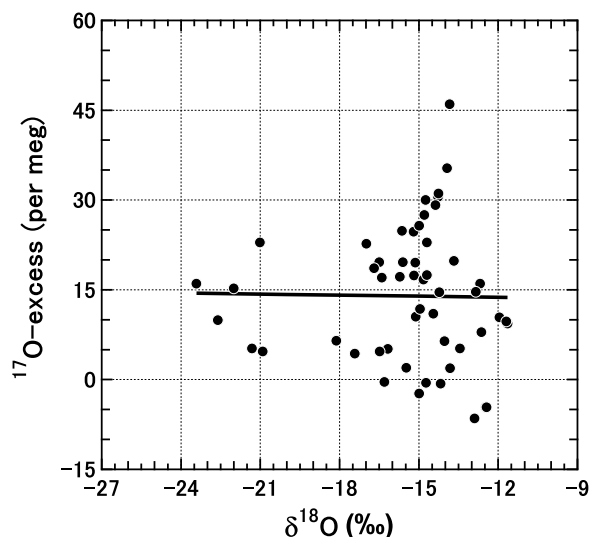
[19] In principle, an optimal value of  $^{18}\alpha_{\text{diff}}$  can be estimated in similar ways from d-excess data. Using the d-excess obtained by Uemura *et al.* [2008] for the same samples and the recently published values for  $^{2}\alpha_{\text{diff}}$ / $^{18}\alpha_{\text{diff}}$  [Luz *et al.*, 2009], we calculated  $^{18}\alpha_{\text{diff}}$  as  $1.0070 \pm 0.0013$ . This value is smaller than that obtained by  $^{17}\text{O}$ -excess, but the difference is within the estimation error. It is interesting to note, that our estimated values of  $^{18}\alpha_{\text{diff}}$  based on the  $^{17}\text{O}$ -excess and d-excess data are similar to the one (1.0076) obtained by Pfahl and Wernli [2009] from the d-excess data of water vapor at Rehovot (Israel) using Lagrangian simulations. Importantly, Pfahl and Wernli [2009] also estimated the optimal value of  $^{18}\alpha_{\text{diff}}$  independently of wind speed. In summary, the above results strongly suggest that the relationship of MJ79 between wind-speed and  $\alpha_{\text{diff}}$  cannot be applied in the case of evaporation from the ocean. In addition, the value of  $^{18}\alpha_{\text{diff}}$  that best fits natural conditions in the open sea is larger than generally thought.

### 4.3. Validity of the Closure Assumption

[20] In the calculations above (equation (2)), we assumed that the sole source of moisture in the Atmospheric Boundary Layer (ABL), in which we took our samples, is local evaporation (the so called "closure assumption") [Merlivat and Jouzel, 1979]. However, this is an over simplification of real world situations because the vapor in the ABL is likely mixed with moisture depleted in heavy isotopes from higher elevations in the atmosphere [He and Smith, 1999]. For example, by using a general circulation model (GCM), which does not include the closure assumption, Jouzel and Koster [1996] predicted smaller  $\delta^{18}\text{O}$  of ABL vapor than values predicted using the closure assumption ( $\delta^{18}\text{O}_{\text{closure}}$ ). The  $\delta^{18}\text{O}$  difference ( $\delta^{18}\text{O}_{\text{closure}} - \delta^{18}\text{O}_{\text{GCM}}$ ) between  $20^\circ\text{S}$  to  $50^\circ\text{S}$  showed gradual increase from 2‰ to 6‰ because  $\delta^{18}\text{O}$  at high elevations becomes smaller with increasing latitude. Similarly, Angert *et al.* [2008] suggested that the seasonal cycle of vapor isotopic compositions at Rehovot, Israel, is influenced by vertical mixing across the top of the ABL. The important question for the present study is whether similar mixing would significantly modify  $^{17}\text{O}$ -excess in the ABL.

[21] At present there is no simple answer to the above question because there are no observations of  $^{17}\text{O}$ -excess in vapor from high elevations. Our data set suggests that while mixing of moisture depleted in  $^{18}\text{O}$  has strong effect on  $\delta^{18}\text{O}$ , it does not increase the  $^{17}\text{O}$ -excess. In Figure 3 we plotted  $^{17}\text{O}$ -excess vs.  $\delta^{18}\text{O}$  and, as can be seen, the correlation between them is statistically insignificant ( $R^2 = 0.04$ ). In particular, six data points have  $\delta^{18}\text{O}$  smaller than  $-20\%$ . These values were measured on samples from near the Antarctic coast ( $65^\circ\text{S}$ ) and most probably indicate mixing of  $\delta^{18}\text{O}$  depleted moisture from aloft. Nevertheless, Figure 3 shows that this mixing did not increase nor decrease the  $^{17}\text{O}$ -excess. Therefore, the simple closure assumption appears to work well in explaining the origin of the  $^{17}\text{O}$ -excess in marine vapor of our observation.

[22] In principle,  $^{17}\text{O}$ -excess of atmospheric vapor could increase by partial non equilibrium evaporation of falling rain drops just as  $^{17}\text{O}$ -excess increases during evaporation from the ocean. An increase in  $^{17}\text{O}$ -excess of atmospheric moisture will occur only if rain drops partially evaporate.



**Figure 3.** The  $^{17}\text{O}$ -excess versus  $\delta^{18}\text{O}$  of vapor. The solid line indicates statistically insignificant linear regression.

Because, rain evaporation is known to recycle significant fraction of precipitation [Worden et al., 2007], this possibility must be considered. It would be desirable to study the extent to which rain evaporation affects the  $^{17}\text{O}$ -excess of vapor by direct measurements in future research.

## 5. Conclusions

[23] Vapor above the ocean surface has an excess of  $^{17}\text{O}$  with respect to vapor in equilibrium with seawater, and there is negative correlation between the  $^{17}\text{O}$ -excess and  $h_p$ . This result is consistent with the Craig-Gordon concept and suggests that the  $^{17}\text{O}$ -excess is controlled by kinetic fractionation during evaporation. The obtained data gave evidence that relative humidity over the ocean is the main controlling factor for  $^{17}\text{O}$ -excess. Therefore,  $^{17}\text{O}$ -excess should be very useful for constraining oceanic humidity in hydrological and climatic models.

[24] We determined  $^{18}\alpha_{\text{diff}}$  values for individual data points using the measured  $^{17}\text{O}$ -excess with a Craig-Gordon formulation. The calculated  $^{18}\alpha_{\text{diff}}$  are scattered, and do not show clear dependency on wind-speed. Since the inclusion of possible wind speed effect does not significantly improve the modeled values, we suggest the universal optimized value of  $^{18}\alpha_{\text{diff}}$  (1.008) for evaporation at natural oceanic conditions. The new value of  $^{18}\alpha_{\text{diff}}$  is larger than the most widely accepted figure ( $\sim 1.005$ ) of Merlivat and Jouzel [1979], which is based on wind-tunnel experiments.

[25] We cannot completely rule out effects of mixing of air from high elevations into the ABL on the  $^{17}\text{O}$ -excess there. However, our observations suggest that such effect, if any, should be small. In order to reduce the uncertainty in  $^{18}\alpha_{\text{diff}}$ , it would be desirable to obtain data on the vertical distribution of  $^{17}\text{O}$ -excess in atmospheric profiles.

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