

## ■ Mass-dependent triple oxygen isotope variations in terrestrial materials

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### ■ Supplementary Information

The Supplementary Information includes:

- Fractionation Equations
- The Terrestrial Fractionation Line and the Definition of  $\Delta^{17}\text{O}$
- Figures S-1 to S-3
- Supplementary Information References

### *Fractionation Equations*

Light stable isotope variability is caused by a preferential enrichment of one or more isotopes between coexisting phases. This can be due to either equilibrium processes or kinetic processes – such as evaporation into undersaturated air. The fundamental equation quantifying fractionation between two phases *a* and *b* is

$$\alpha = \frac{R_a}{R_b} \quad \text{Eq. S-1}$$

where *R* is the ratio of the heavy to light isotope, such as  $^{18}\text{O}/^{16}\text{O}$  or  $^{17}\text{O}/^{16}\text{O}$ . In delta notation

$$\delta = \left( \frac{R_x}{R_s} - 1 \right) 1000 \quad \text{Eq. S-2}$$

and the  $\alpha$  value is given by

$$\alpha_{a-b} = \frac{\delta_a + 1000}{\delta_b + 1000} \quad \text{Eq. S-3}$$



For the three isotope system, the triple isotope fractionation exponent  $\theta_{a-b}$  has been introduced given by

$$\alpha^{17}\text{O}_{a-b} = (\alpha^{18}\text{O}_{a-b})^\theta \quad \text{Eq. S-4}$$

The  $\theta$  value is not constant. It changes with fractionation process (e.g., kinetic, equilibrium) (Matsuhisa *et al.*, 1978; Young *et al.*, 2002). For equilibrium processes,  $\theta$  varies regularly with temperature (Pack and Herwartz, 2014; Sharp *et al.*, 2016). Eq. S-4 can be recast in a linear form as

$$\ln(\alpha^{17}\text{O}) = \theta \ln(\alpha^{18}\text{O}) \quad \text{Eq. S-5}$$

A similar relationship can be made using linearised delta values in per mil notation, where the  $\delta'$  (delta-prime) is defined as (Miller, 2002)

$$\delta' = 1000 \ln\left(\frac{\delta}{1000} + 1\right) \quad \text{Eq. S-6}$$

In  $\delta'$  notation,  $\theta_{a-b}$  is given by

$$\theta_{a-b} = \frac{\delta'^{17}\text{O}_a - \delta'^{17}\text{O}_b}{\delta'^{18}\text{O}_a - \delta'^{18}\text{O}_b} \quad \text{Eq. S-7}$$

## The Terrestrial Fractionation Line and the Definition of $\Delta'^{17}\text{O}$

The  $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$  values of terrestrial materials define the 'Terrestrial Fractionation Line' (TFL) with a slope of  $\sim 1/2$ . The general expression for the TFL is

$$\delta'^{17}\text{O} = \lambda_{\text{RL}} \delta'^{18}\text{O} + \gamma_{\text{RL}} \quad \text{Eq. S-8}$$

$\theta$  is replaced by  $\lambda_{\text{RL}}$  (RL is for reference line) to signify that the best-fit slope is strictly empirical and does not have thermodynamic significance. The  $\gamma_{\text{RL}}$  is the  $y$ -intercept of the best fit line, often taken as 0‰. With ever-higher precision,  $\lambda_{\text{RL}}$  values (*i.e.*, the slope of the TFL) have been refined, with published slopes ranging from 0.515 to 0.5305. There is no 'correct' TFL slope, as different equilibrium or kinetic processes result in slightly different triple isotope fractionations. For example, meteoric waters fall on a trend that does not overlap with the trend defined by most rocks and minerals (Luz and Barkan, 2010; Pack and Herwartz, 2014; Pack *et al.*, 2016). A  $\delta'^{17}\text{O}$  -  $\delta'^{18}\text{O}$  plot of published data from natural samples is shown in Figure S-1. The  $\lambda$  and  $\gamma$  values differ slightly for different materials, but virtually all data plot exactly on the same line at the resolution of the figure.

In order to better visualise small deviations from the TFL reference line, the  $\Delta'^{17}\text{O}$  value has been introduced. The  $\Delta'^{17}\text{O}$  term is defined as

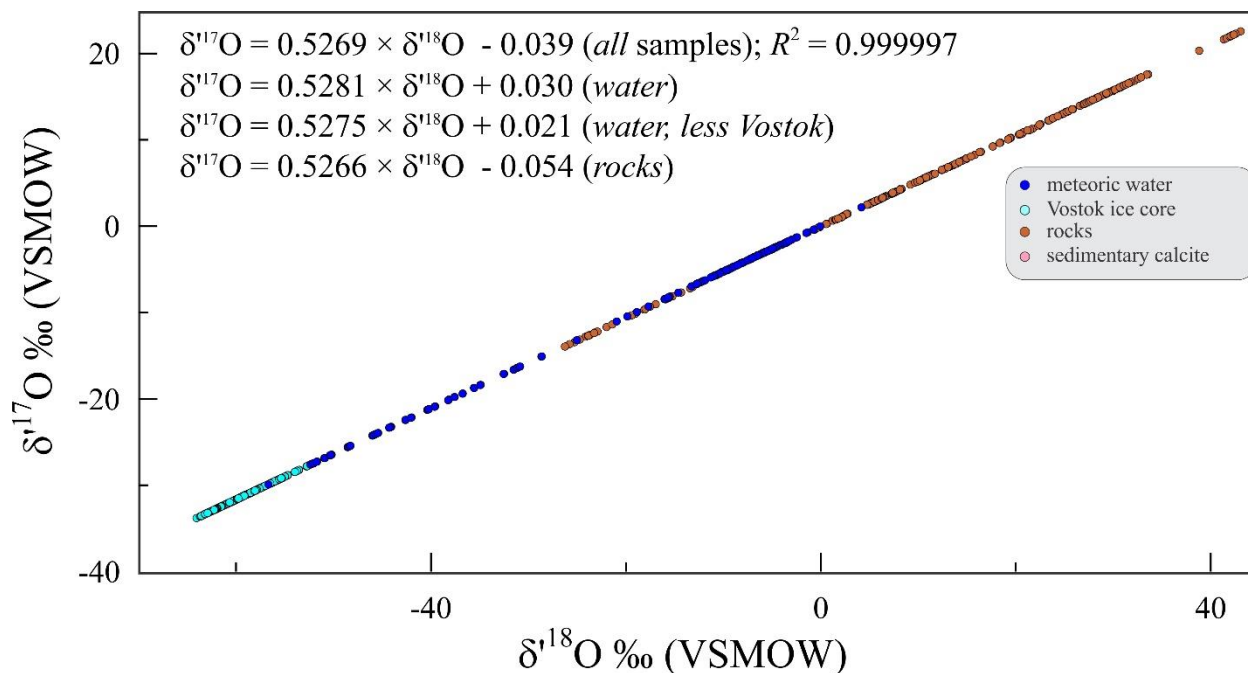
$$\Delta'^{17}\text{O} = \delta'^{17}\text{O} - \lambda_{\text{RL}} \delta'^{18}\text{O} + \gamma_{\text{RL}} \quad \text{Eq. S-9}$$



Often,  $\lambda_{\text{RL}}$  is taken as the best-fit slope  $\lambda$  for a set of data in  $\delta^{17}\text{O} - \delta^{18}\text{O}$  space and  $\gamma_{\text{RL}}$  is the intercept (generally assumed to be 0). In this study,  $\Delta^{17}\text{O}$  values from different publications are normalised to VSMOW (rocks and minerals) and VSMOW/SLAP2 scale (waters; SLAP2 from (Schoenemann *et al.*, 2013)) and derived  $\Delta^{17}\text{O}$  to a reference line with slope 0.528 and zero intercept. Rock samples are normalised to the VSMOW scale with the  $\Delta^{17}\text{O}$  value of the broadly adopted San Carlos Olivine standard (SCO) having a  $\Delta^{17}\text{O}$  value of -0.05‰ (Sharp *et al.*, 2016) relative to a  $\lambda_{\text{RL}} = 0.528$  (zero intercept).

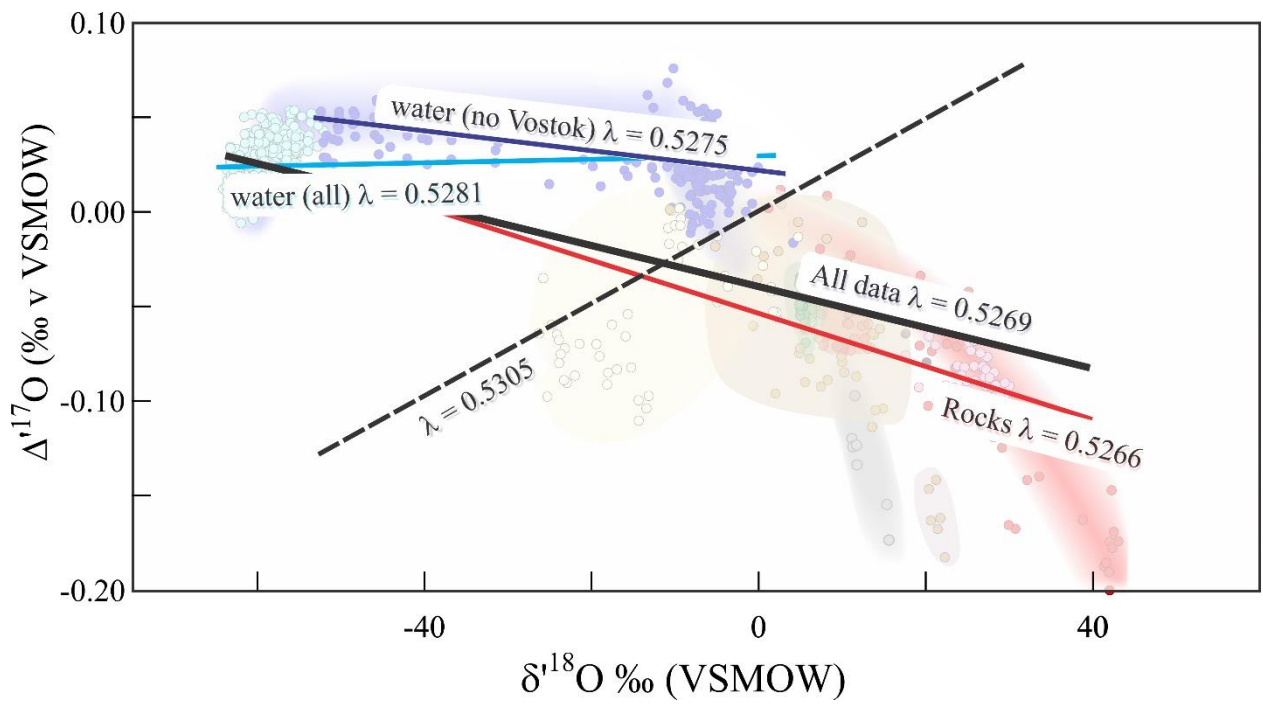


## Supplementary Figures



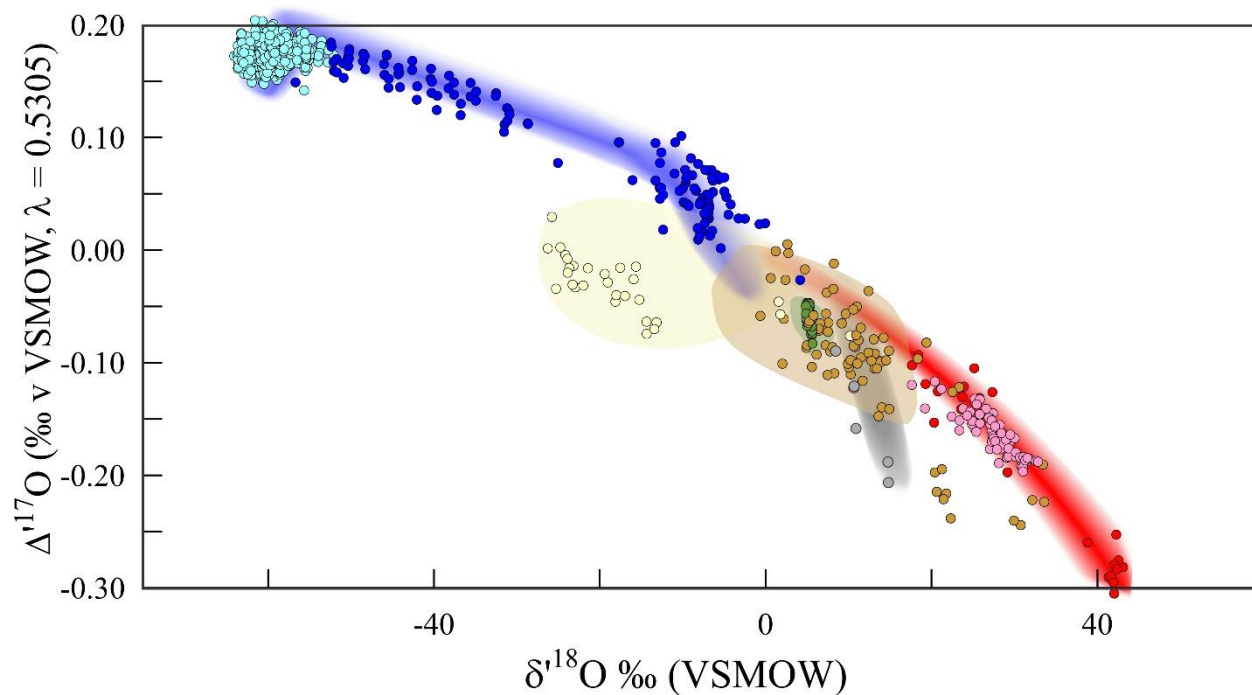
**Figure S-1**  $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$  plot of terrestrial materials (Terrestrial Fractionation Line). All data plot on a line with a slope of 0.5269. The best fit is strongly anchored by the large number of extremely light ice samples from the Vostok core. Excluding these samples, the best-fit line for waters has a slope ( $\lambda$  value) of 0.5275. Rocks have a slightly lower slope of 0.5266. The best fit to the rock data is strongly controlled by low temperature marine sediments. Clearly, there is no single  $\lambda$  value that is characteristic of all terrestrial materials. (Note: Samples affected by photochemical reactions are not considered, as they can fall well off the typical TFL). Data from the following sources: (Landais *et al.*, 2006, 2008, 2010; Rumble *et al.*, 2007, 2013; Luz and Barkan, 2010; Levin *et al.*, 2014; Pack and Herwartz, 2014; Herwartz *et al.*, 2015; Li *et al.*, 2015; Sharp *et al.*, 2016 and unpublished data from UNM laboratory). Carbonate data are from J. Wostbrock and were made by total fluorination. Mn-oxide data are from A. Santos and were made by total fluorination.





**Figure S-2** Plot of the  $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$  of characteristic materials with various best-fit lines for different materials. All data are fit with a  $\lambda = 0.5269$ . Waters have a higher  $\lambda$  value while rocks have a lower  $\lambda$  value. The  $\lambda$  value of 0.5305 is the theoretical high-temperature limit (see Fig. S-3).





**Figure S-3**  $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$  plot using a  $\theta = 0.5305$ . The information is identical to that given in Figure 1, but in this plot sample trends have strong negative slopes because the best-fit  $\lambda$  values for natural materials are significantly less than 0.5305. Consequently, there is a general trend of lower  $\Delta^{17}\text{O}$  values with increasing  $\delta^{18}\text{O}$  values that overprints the  $\Delta^{17}\text{O}$  effect of equilibrium and kinetic processes. The total range in  $\Delta^{17}\text{O}$  is larger than in Figure 1, but this is simply a result of the choice of  $\lambda$ , not being a good fit to the data.

## Supplementary Information References

- Herwartz, D., Pack, A., Krylov, D., Xiao, Y., Muehlenbachs, K., Sengupta, S., Di Rocco, T. (2015) Revealing the climate of snowball Earth from  $\Delta^{17}\text{O}$  systematics of hydrothermal rocks. *Proceedings of the National Academy of Sciences* 112, 5337-5341.
- Landais, A., Barkan, E., Yakir, D., Luz, B. (2006) The triple isotopic composition of oxygen in leaf water. *Geochimica et Cosmochimica Acta* 70, 4105-4115.
- Landais, A., Barkan, E., Luz, B. (2008) Record of  $\delta^{18}\text{O}$  and  $^{17}\text{O}$ -excess in ice from Vostok Antarctica during the last 150,000 years. *Geophysical Research Letters* 35.
- Landais, A., Risi, C., Bony, S., Vimeux, F., Descroix, L., Falourd, S., Bouygues, A. (2010) Combined measurements of  $^{17}\text{O}$ -excess and  $d$ -excess in African monsoon precipitation: Implications for evaluating convective parameterizations. *Earth and Planetary Science Letters* 298, 104-112.
- Levin, N.E., Raub, T.D., Dauphas, N., Eiler, J.M. (2014) Triple oxygen isotope variations in sedimentary rocks. *Geochimica et Cosmochimica Acta* 139, 173-189.
- Li, S., Levin, N.E., Chesson, L.A. (2015) Continental scale variation in  $^{17}\text{O}$ -excess of meteoric waters in the United States. *Geochimica et Cosmochimica Acta* 164, 110-126.
- Luz, B., Barkan, E. (2010) Variations of  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  in meteoric waters. *Geochimica et Cosmochimica Acta* 74, 6276-6286.
- Matsuhisa, Y., Goldsmith, J.R., Clayton, R.N. (1978) Mechanisms of hydrothermal crystallization of quartz at 250°C and 15 kbar. *Geochimica et Cosmochimica Acta* 42, 173-182.
- Miller, M.F. (2002) Isotopic fractionation and the quantification of  $^{17}\text{O}$  anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochimica et Cosmochimica Acta* 66, 1881-1889.
- Pack, A., Herwartz, D. (2014) The triple oxygen isotope composition of the Earth mantle and  $\Delta^{17}\text{O}$  variations in terrestrial rocks. *Earth and Planetary Science Letters* 390, 138-145.
- Pack, A., Tanaka, R., Hering, M., Sengupta, S., Peters, S., Nakamura, E. (2016) The oxygen isotope composition of San Carlos olivine on the VSMOW2-SLAP2 scale. *Rapid Communications in Mass Spectrometry* 30, 1495-1504.
- Rumble, D.I., Miller, M.F., Franchi, I.A., Greenwood, R.C. (2007) Oxygen three-isotope fractionation lines in terrestrial silicate minerals: An inter-laboratory comparison of hydrothermal quartz and eclogitic garnet. *Geochimica et Cosmochimica Acta* 71, 3592-3600.
- Rumble, D., Bowring, S., Iizuka, T., Komiya, T., Lepland, A., Rosing, M.T., Ueno, Y. (2013) The oxygen isotope composition of Earth's oldest rocks and evidence of a terrestrial magma ocean. *Geochemistry, Geophysics, Geosystems* 14, 1929-1939.
- Schoenemann, S.W., Schauer, A.J. and Steig, E.J. (2013) Measurement of SLAP2 and GISP  $\delta^{17}\text{O}$  and proposed VSMOW-SLAP normalization for  $\delta^{17}\text{O}$  and  $^{17}\text{O}$ -excess. *Rapid Communications in Mass Spectrometry* 27, 582-590.
- Sharp, Z.D., Gibbons, J.A., Maltsev, O., Atudorei, V., Pack, A., Sengupta, S., Shock, E.L., Knauth, L.P. (2016) A calibration of the triple oxygen isotope fractionation in the  $\text{SiO}_2$  -  $\text{H}_2\text{O}$  system and applications to natural samples. *Geochimica et Cosmochimica Acta* 186, 105-119.
- Young, E.D., Galy, A., Nagahara, H. (2002) Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochimica et Cosmochimica Acta* 66, 1095-1104.

