Mass-dependent triple oxygen isotope variations in terrestrial materials

Z.D. Sharp, J.A.G. Wostbrock, A. Pack

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

$$\alpha = \frac{R_a}{R_b}$$  \hspace{1cm} \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

$$\delta = \left( \frac{R_a}{R_i} - 1 \right) \times 1000$$  \hspace{1cm} \text{Eq. S-2}

and the $\alpha$ value is given by

$$\alpha_{a-b} = \frac{\delta_a + 1000}{\delta_b + 1000}$$  \hspace{1cm} \text{Eq. S-3}
For the three isotope system, the triple isotope fractionation exponent $\theta_{a-b}$ has been introduced given by

$$\alpha^{17}O_{a-b} = (\alpha^{18}O_{a-b})^\theta$$  \hspace{1cm} \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

$$\ln(\alpha^{17}O) = \theta \ln(\alpha^{18}O)$$  \hspace{1cm} \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)

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

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

$$\theta_{a-b} = \frac{\delta^{17}O_a - \delta^{17}O_b}{\delta^{18}O_a - \delta^{18}O_b}$$  \hspace{1cm} \text{Eq. S-7}$$

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

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

$$\delta^{17}O = \lambda_{RL} \delta^{18}O + \gamma_{RL}$$  \hspace{1cm} \text{Eq. S-8}$$

$\theta$ is replaced by $\lambda_{RL}$ (RL is for reference line) to signify that the best-fit slope is strictly empirical and does not have thermodynamic significance. The $\gamma_{RL}$ is the $y$-intercept of the best fit line, often taken as 0‰. With ever-higher precision, $\lambda_{RL}$ 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 $\delta^{17}O$ - $\delta^{18}O$ 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 $\Delta'^{17}O$ value has been introduced. The $\Delta'^{17}O$ term is defined as

$$\Delta'^{17}O = \delta^{17}O - \lambda_{RL} \delta^{18}O + \gamma_{RL}$$  \hspace{1cm} \text{Eq. S-9}$$
Often, $\lambda_{RL}$ is taken as the best-fit slope $\lambda$ for a set of data in $\delta^{17}O - \delta^{18}O$ space and $\gamma_{RL}$ is the intercept (generally assumed to be 0). In this study, $\Delta^{17}O$ values from different publications are normalised to VSMOW (rocks and minerals) and VSMOW/SLAP2 scale (waters; SLAP2 from Schoenemann et al., 2013) and derived $\Delta^{17}O$ to a reference line with slope 0.528 and zero intercept. Rock samples are normalised to the VSMOW scale with the $\Delta^{17}O$ value of the broadly adopted San Carlos Olivine standard (SCO) having a $\Delta^{17}O$ value of -0.05‰ (Sharp et al., 2016) relative to a $\lambda_{RL} = 0.528$ (zero intercept).
Supplementary Figures

Figure S-1 $\delta^{18}O$-$\delta^{17}O$ 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 $\delta^{18}$O-$\Delta^{17}$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  $\delta^{18}$O-$\Delta^{17}$O plot using a $\lambda = 0.5305$. 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 $\Delta^{17}$O values with increasing $\delta^{18}$O values that overprints the $\Delta^{17}$O effect of equilibrium and kinetic processes. The total range in $\Delta^{17}$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


