

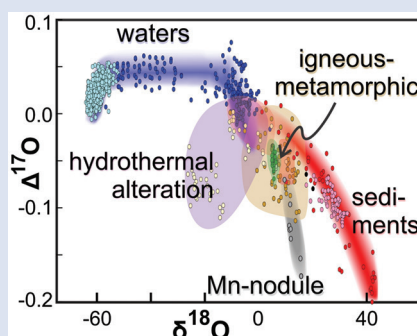
Mass-dependent triple oxygen isotope variations in terrestrial materials

Z.D. Sharp¹, J.A.G. Wostbrock¹, A. Pack²



doi: 10.7185/geochemlet.1815

Abstract



High precision triple oxygen isotope analyses of terrestrial materials show distinct fields and trends in $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space that can be explained by well understood fractionation processes. The $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ field for meteoric waters has almost no overlap with that of rocks. Globally, meteoric water defines a λ value of ~ 0.528 , although a better fit to waters with $\delta^{18}\text{O}$ values > -20 ‰ is $\delta^{17}\text{O} = 0.52654 (\pm 0.00036) \delta^{18}\text{O} + 0.014 (\pm 0.003)$. Low temperature marine sediments define a unique and narrow band in $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space with high $\delta^{18}\text{O}$ and low $\Delta^{17}\text{O}$ values explained by equilibrium fractionation. Hydrothermal alteration shifts the rock composition to lower $\delta^{18}\text{O}$ values at low fluid/rock ratios, and finally higher $\Delta^{17}\text{O}$ when F/R ratios are greater than 1. In order to make the triple isotope data tractable to the entire geological community, consensus on a reporting scheme for $\Delta^{17}\text{O}$ is desirable. Adoption of $\lambda_{\text{RL}} = 0.528$ (λ_{RL} = slope of $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ reference line, the 'Terrestrial Fractionation Line' or TFL) would bring the 'rock' community

in line with well established hydrological reporting conventions.

Received 10 February 2018 | Accepted 5 May 2018 | Published 1 June 2018

Introduction

The early practitioners of stable isotope geochemistry recognised that the three isotopes of oxygen followed mass-dependent rules, such that fractionation in $^{17}\text{O}/^{16}\text{O}$ was approximately half that of $^{18}\text{O}/^{16}\text{O}$ for both equilibrium and kinetic processes (Craig, 1957). Measuring the $^{17}\text{O}/^{16}\text{O}$ ratios therefore provided no additional information to the $^{18}\text{O}/^{16}\text{O}$ values alone. Mass-independent fractionations have since been found in primitive meteorites (Clayton *et al.*, 1973) and many atmospheric components such as O_3 , CO_2 , H_2O_2 which are explained by photochemical processes (Thiemens, 2006).

With improved precision, it is now recognised that there are small, but non-zero deviations from a simple best fit line in $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space that are related to mass-dependent processes (Luz and Barkan, 2010; Pack and Herwartz, 2014). As more data are collected, general trends are being observed. Here we compile the bulk of published, and our own unpublished, high precision triple oxygen isotope data and categorise distinct trends in $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space for different processes.

The Terrestrial Fractionation Line and Relevant Notation

A fit through $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ values of terrestrial materials defines the 'Terrestrial Fractionation Line' (TFL) with a slope of ~ 0.5 .

The general expression for the TFL is

$$\delta^{17}\text{O} = \lambda_{\text{TFL}} \delta^{18}\text{O} + \gamma_{\text{TFL}} \quad \text{Eq. 1}$$

where λ_{TFL} is the best fit slope and γ_{TFL} is the y -intercept of the best fit line. Equation 1 and all data in this study are presented in the linearised notation given by δ' (see Miller, 2002 and Supplementary Information). There is no 'correct' or unique TFL, as different equilibrium or kinetic processes result in slightly different triple isotope fractionations. For example, meteoric waters fall on a trend that does not exactly 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. Virtually all data plot exactly on the same line at the resolution of the figure.

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

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda_{\text{RL}} \delta^{18}\text{O} + \gamma_{\text{RL}} \quad \text{Eq. 2}$$

λ_{RL} is the reference line slope and γ_{RL} is the y intercept. In this study, $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ 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 (λ_{RL}) and zero intercept ($\gamma_{\text{RL}} = 0$). 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 $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of 5.4 ‰ and -0.05 ‰ relative to a $\lambda_{\text{RL}} = 0.528$ and $\gamma_{\text{RL}} = 0$ (Sharp *et al.*, 2016). See Pack *et al.* (2016) for details of normalisation.

1. University of New Mexico, Albuquerque, NM 87131, USA

2. Georg-August-Universität, Göttingen, D-37073, Germany

* Corresponding author (email: zsharp@unm.edu)



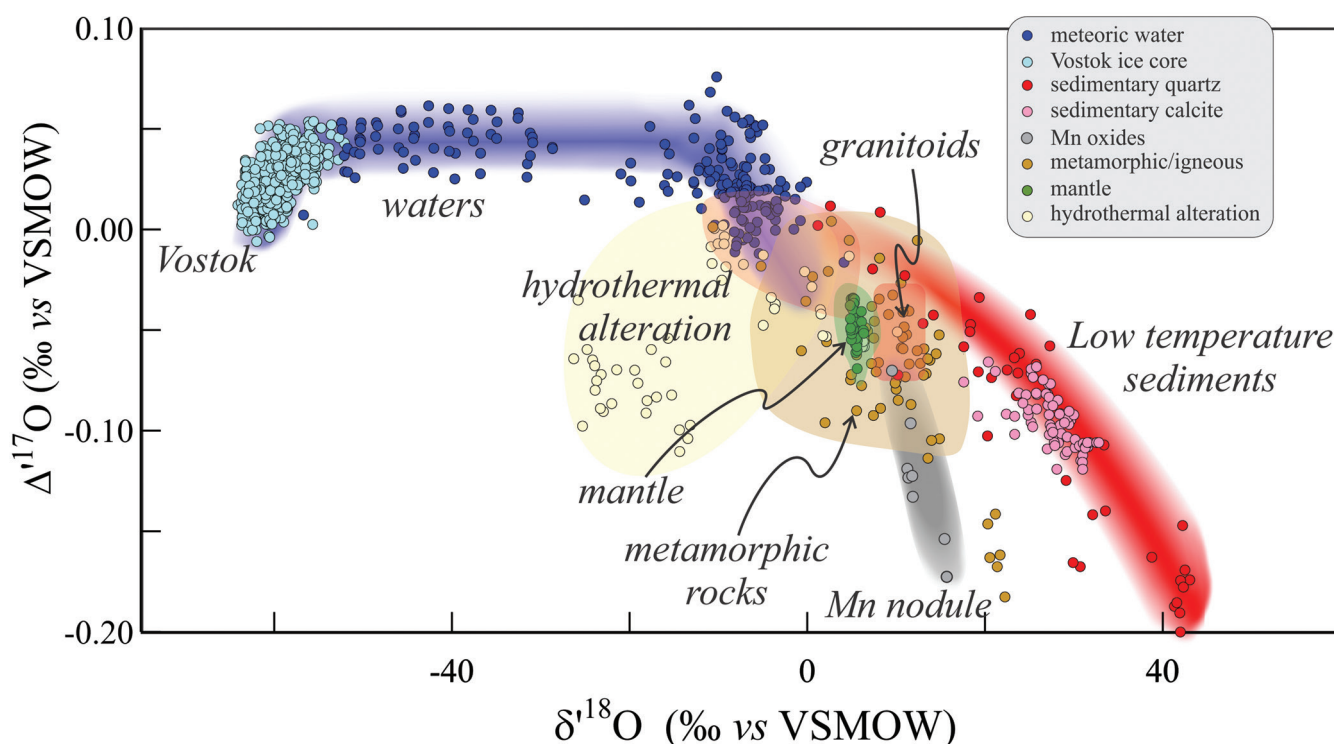


Figure 1 Characteristic $\delta^{18}\text{O}$ – $\Delta^{17}\text{O}$ fields for different materials. Meteoric waters have uniquely high $\Delta^{17}\text{O}$ values and generally low $\delta^{18}\text{O}$ values. Marine carbonates and silica plot in a narrow band of high $\delta^{18}\text{O}$ and low $\Delta^{17}\text{O}$ values. Manganese oxides have unusually low $\Delta^{17}\text{O}$ values due to incorporation of dissolved O_2 . Hydrothermal alteration drives igneous and metamorphic rocks to lower $\delta^{18}\text{O}$ values. All data are standardised to VSMOW, where solid samples are normalised to $\Delta^{17}\text{O}$ of San Carlos olivine = -0.05 ‰. See Figure S-1 for data sources.

Small variations in $\Delta^{17}\text{O}$ become apparent in a $\Delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ plot (Fig. 1). Waters have positive $\Delta^{17}\text{O}$ values, while rock samples have negative $\Delta^{17}\text{O}$ values that tend to decrease with increasing $\delta^{18}\text{O}$. Hydrothermally altered samples have the lowest $\delta^{18}\text{O}$ values of any rock samples.

Characteristic $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ Fields and Trends

A number of generalisations can be made from the data shown in Figure 1. A clear separation in the $\Delta^{17}\text{O}$ values between waters and rocks is immediately apparent. The mantle has a very tight range of $\Delta^{17}\text{O}$ values of -0.03 to -0.07 ‰, with most samples plotting at -0.05 ± 0.01 ‰. The 0.04 spread in $\Delta^{17}\text{O}$ in mantle samples is due to mantle metasomatism or alteration and in some cases analytical error. True variability within pristine mantle is likely much smaller and is centered on $\Delta^{17}\text{O} = -0.05$ ‰.

The $\delta^{18}\text{O}$ values of more evolved high silica igneous rocks are higher than the typical mantle value of ~ 5.4 ‰, but the $\Delta^{17}\text{O}$ values remain relatively constant. This is because 1) the shift in $\delta^{18}\text{O}$ is small and 2) the associated high- T θ value (where $\theta = \ln(\alpha^{17}\text{O}) / \ln(\alpha^{18}\text{O})$; see Supplementary Information) for minerals and melts is close to the reference slope value of 0.528 , thereby moving more siliceous samples to higher $\delta^{18}\text{O}$, but constant $\Delta^{17}\text{O}$ values.

Meteoric waters. Meteoric water data vary greatly in $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space (Fig. 2). Samples with $\delta^{18}\text{O}$ values between -55 and -15 ‰ have an average $\Delta^{17}\text{O}$ value of 0.041 ± 0.006 and fall on a line with slope $\lambda = 0.528$. The offset in $\Delta^{17}\text{O}$ relative to the value of 0 ‰ for the ocean is related to the kinetic fractionation associated by transport of vapour from the saturated layer into the free, undersaturated atmosphere

(Luz and Barkan, 2010). Samples from the Vostok ice core (pale blue points in Fig. 2) are fit with a higher λ value of 0.5309 ± 0.0001 , which is attributed loosely to variable humidity and wind speed at the ocean source and supersaturation conditions during condensation in extremely cold environments (Landais *et al.*, 2008) or direct condensation as ‘diamond dust’ (Miller, 2018). For $\delta^{18}\text{O}$ values greater than -20 ‰, the $\Delta^{17}\text{O}$ values of meteoric waters show the reverse trend, decreasing with increasing $\delta^{18}\text{O}$. Rain re-evaporation and mixing have been explained as the principle driving force towards the low $\Delta^{17}\text{O}$ values (Landais *et al.*, 2010; Risi *et al.*, 2013; Li *et al.*, 2015).

The best fit line to meteoric water samples with a $\delta^{18}\text{O}$ value greater than -20 ‰ is

$$\delta^{17}\text{O} = 0.52654 (\pm 0.00036) \delta^{18}\text{O} + 0.014 (\pm 0.003). \text{ Eq. 3}$$

Most waters outside of extreme polar regions have $\delta^{18}\text{O}$ values that are greater than -20 ‰, so that Equation 3 is a rough fit to the Global Meteoric Water Line for waters from non-polar sample regions.

Low temperature sediments. A compilation of data from low temperature sediments shows decreasing $\Delta^{17}\text{O}$ values with increasing $\delta^{18}\text{O}$ (Fig. 3). This trend is explained by the temperature effect on the equilibrium fractionation between minerals and seawater. The triple isotope equilibrium θ value decreases with decreasing temperature, (Cao and Liu, 2011; Sharp *et al.*, 2016). The curved line in Figure 3 is the equation governing the $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ values of silica in equilibrium with ocean water as a function of temperature (Sharp *et al.*, 2016). Most marine silica samples fall on or near this curved line. Samples that have equilibrated with meteoric waters consequently plot towards lower $\delta^{18}\text{O}$ and, in general, higher $\Delta^{17}\text{O}$ values, consistent with a lighter meteoric water source. Our unpublished manganese oxide data from a deep sea nodule off Hawaii have very low $\Delta^{17}\text{O}$ values in relation to

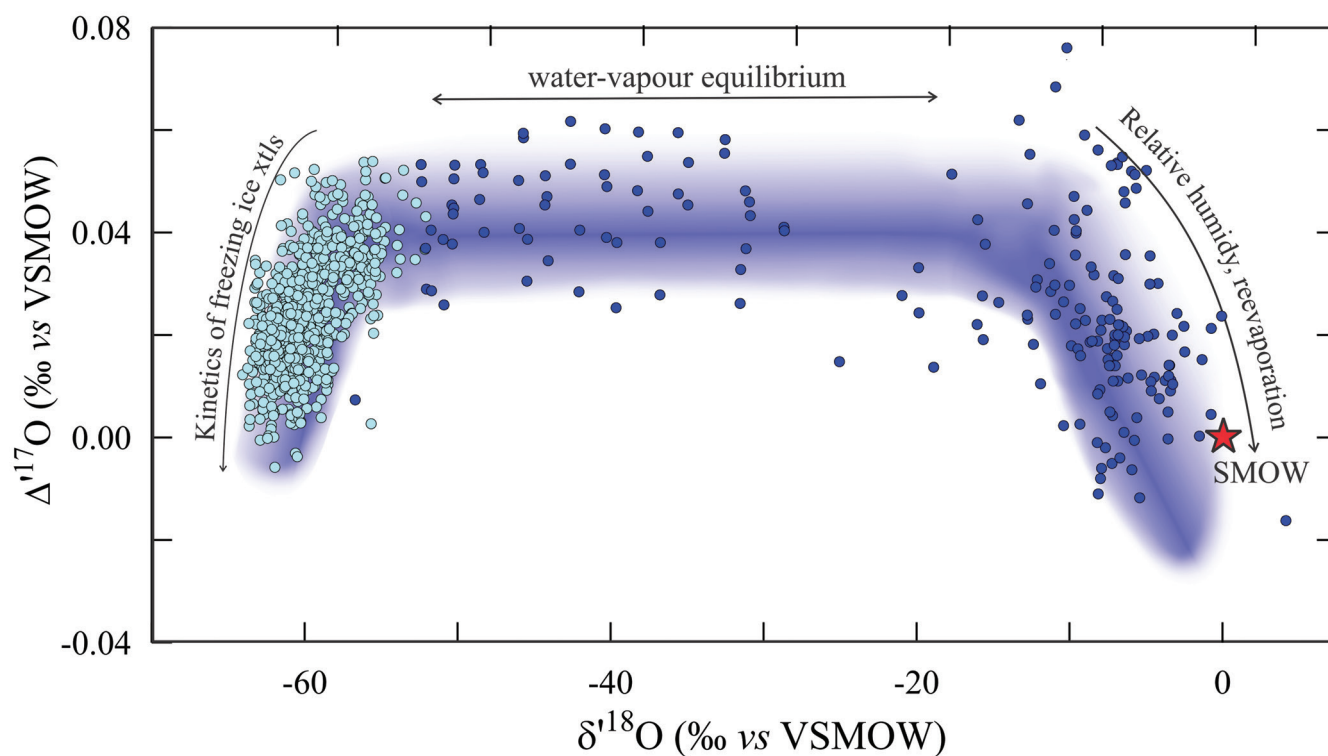


Figure 2 $\delta^{18}\text{O} - \Delta^{17}\text{O}$ values of meteoric waters. Waters can be divided into three segments: extreme low values with a λ of 0.5309 (Vostok ice core - pale blue symbols); light waters with $\delta^{18}\text{O}$ values between -60 and -30 ‰ from high latitudes and a λ of 0.528; and heavier waters (>-20 ‰) with a best fit λ of 0.5263.

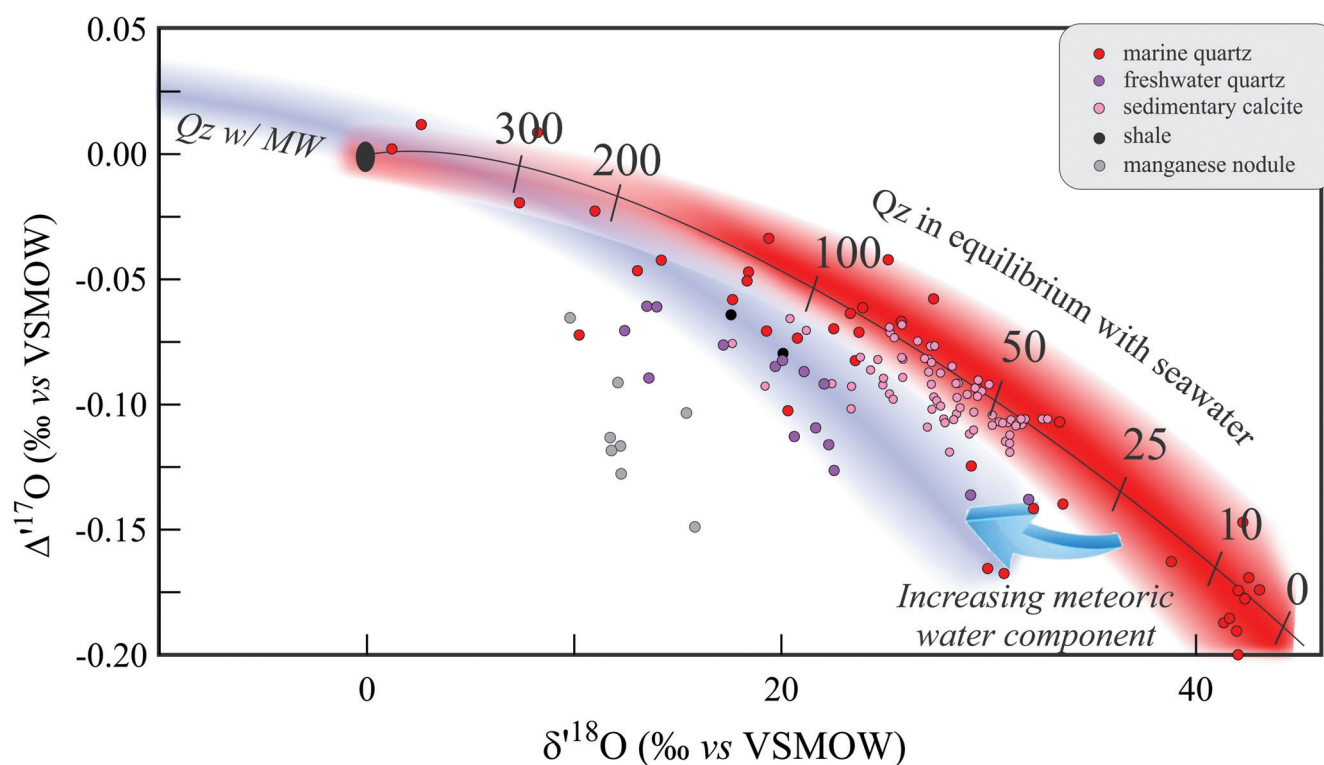


Figure 3 $\delta^{18}\text{O} - \Delta^{17}\text{O}$ plot of sedimentary materials. The red silica samples equilibrated with ocean water plot along the equilibrium fractionation curved line (Sharp *et al.*, 2016) (tick marks indicate equilibrium temperature). Samples equilibrated with meteoric water plot to the left of the marine data, consistent with a lower $\delta^{18}\text{O}$ and higher $\Delta^{17}\text{O}$ water value. Manganese oxide data plot with anomalously low $\Delta^{17}\text{O}$ values, suggestive of incorporation of dissolved O_2 (Mandernack *et al.*, 1995).

their $\delta^{18}\text{O}$ values, explained by incorporation of dissolved air O_2 into the MnO_2 structure ($\Delta^{17}\text{O}_{\text{air}} = -0.41$ to -0.45). The low $\Delta^{17}\text{O}$ values support the conclusion that dissolved O_2 is directly incorporated in manganates during biogenic and abiogenic laboratory synthesis experiments (Mandernack *et al.*, 1995).

Hydrothermal mixing. A number of variables control the isotopic effect during hydrothermal alteration, including temperature, initial rock protolith and fluid compositions, and fluid/rock (F/R) ratio. Nevertheless, the $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ field of most hydrothermally altered rock is surprisingly limited.

Hydrothermal alteration is modelled using a simple mass balance mixing equation. A fraction of water is allowed to equilibrate with a rock at a given temperature. The bulk composition is given by

$$\delta^{18}\text{O}_{\text{bulk}} = X_{\text{water}} (\delta^{18}\text{O}_{\text{water initial}}) + (1-X_{\text{water}}) (\delta^{18}\text{O}_{\text{rock initial}}) \\ = X_{\text{water}} (\delta^{18}\text{O}_{\text{water final}}) + (1-X_{\text{water}}) (\delta^{18}\text{O}_{\text{rock final}}) \quad \text{Eq. 4}$$

The final $\delta^{18}\text{O}$ value of the rock is determined by the additional fractionation equation

$$\alpha = \frac{1000 + \delta_{\text{final rock}}}{1000 + \delta_{\text{final water}}} \quad \text{Eq. 5}$$

where α varies with temperature.

Mixing calculations are made using the standard delta values. Once the final isotopic compositions are determined, data are linearised for plotting on $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ plots. In linearised plots, mixing trends plot as curved lines.

Figure 4 shows mixing trends between a typical unaltered granitoid ($\delta^{18}\text{O} = 8.5$ ‰; $\Delta^{17}\text{O} = -0.05$ ‰) and meteoric waters of varying composition. Fractionation factors for this example are for quartz. As fluid/rock ratios increase, the delta

values of the altered rock initially move to lower $\delta^{18}\text{O}$ and ultimately higher $\Delta^{17}\text{O}$ values. An extreme example from the 'snowball Earth' altered samples from Karelia (Herwartz *et al.*, 2015) results in $\delta^{18}\text{O}$ values as low as -26 ‰, vastly expanding the hydrothermal alteration field (yellow field in Fig. 4). In more common cases where the $\delta^{18}\text{O}$ value of meteoric water is -20 ‰ or higher, the hydrothermal alteration box is far more limited (red field in Fig. 4).

Assimilation of a high $\delta^{18}\text{O}$ sediment by a granitoid will shift the $\delta^{18}\text{O}$ values higher, and the $\Delta^{17}\text{O}$ values lower (pale blue curve in Fig. 4). In practice, the effect will be small. Even 10 % incorporation of sediment will only move the altered rock as far as the dark blue curve.

General Fields and Choice of λ_{RL}

Figure 1 shows the characteristic $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ regions for different materials. While there is some overlap, different rock types generally plot in distinct regions following well established fractionation rules. The best fit λ value depends on which samples are considered (Fig. S-2). All data have a best fit $\lambda = 0.5269$. Waters define a λ value of 0.5281, but if the light Vostok ice core samples are excluded, the λ becomes 0.5275. Rocks have a still smaller λ value, controlled in large part by the high $\delta^{18}\text{O}$ - low $\Delta^{17}\text{O}$ sedimentary samples.

The isotope community in this nascent field has not reached consensus on a standard reference line - the λ_{RL} value - for calculating $\Delta^{17}\text{O}$ values. We suggest reporting both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ on VSMOW scale. For materials with δ values departing far from zero, one may apply VSMOW/SLAP2 scaling. This ensures that data from the rock and water community remain comparable.

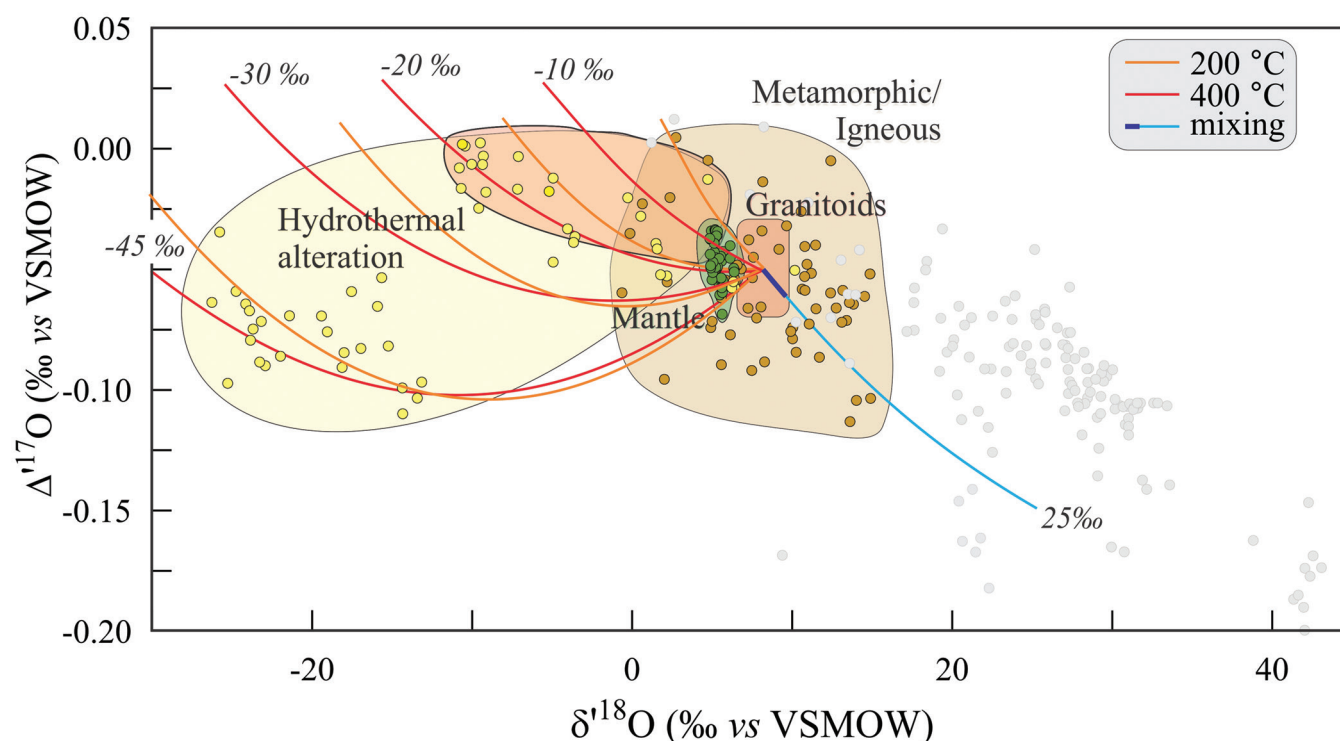


Figure 4 $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ values of hydrothermally altered samples (pale yellow field). Calculated alteration paths are shown for a typical granitoid ($\delta^{18}\text{O} = 8.5$ ‰, $\Delta^{17}\text{O} = -0.05$ ‰) equilibrating with different compositions of meteoric water at 200 °C (orange) and 400 °C (red). The curved line defines different fluid/rock ratios emanating from the initial rock isotope value (F/R = 0). At low fluid/rock ratios, $\delta^{18}\text{O}$ values decrease while $\Delta^{17}\text{O}$ values are essentially unchanged. Only above a fluid/rock ratio of ~ 1 does the $\Delta^{17}\text{O}$ value begin to increase. Most alteration will drive typical granitoids into the limited pale red region. Assimilation of sediments will drive samples in the direction indicated by the blue curve. However, even with 10 % assimilation, the samples will only be shifted the length of the dark blue curve.

The meteorological community uses a λ_{RL} value of 0.528, as this initially had been suggested to be representative of the Global Meteoric Water Line slope (Luz and Barkan, 2010). With such a definition, most rocks have negative $\Delta^{17}\text{O}$ values, whereas meteoric waters generally have positive values. Some studies adopt a $\lambda_{\text{RL}} = 0.5305$, the theoretical θ value at infinite temperature. All natural, equilibrium processes should have θ values less than this value, so that trends for all data should have a negative slope in $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space. In practice, some materials following complex kinetic processes have λ values higher than 0.5305, notably the Vostok ice core data ($\lambda = 0.5309 \pm 0.0002$) and precipitation from Niger (Landais *et al.*, 2010) ($\lambda = 0.543 \pm 0.004$). Most processes undergo fractionation with a θ value (significantly less than 0.5305), resulting in a strong negative trend in $\Delta^{17}\text{O}$ as a function of $\delta^{18}\text{O}$ in this reference frame (Fig. S-3). The adoption of $\lambda_{\text{RL}} = 0.5305$ is consistent with other multiple isotope systems, where the theoretical high-T limit is used as a reference. A $\lambda_{\text{RL}} = 0.528$ would make the 'rock' data compatible with the longstanding data on meteoric waters and would not artificially skew $\Delta^{17}\text{O}$ to more negative values with increasing $\delta^{18}\text{O}$ values. This is critical as researchers combine 'water' and 'rock' data. The authors of this contribution do not agree on a suggested convention.

Conclusions

The $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ values for all terrestrial materials not affected by photochemical effects plot on a straight line with a slope of $\sim 1/2$. In detail, small, purely mass-dependent variations can be resolved and displayed in $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space (Fig. 1). The vast majority of meteoric waters have positive $\Delta^{17}\text{O}$ values, while rocks have negative $\Delta^{17}\text{O}$ values. Low- and high-T rocks fall on distinct trends and fields that can be explained by well understood processes. It is unlikely that many data will fall to the right hand side of the seawater - silica equilibrium curve nor are many rocks expected to fall above the meteoric water line. These may be termed "forbidden" regions. Similarly, samples with $\Delta^{17}\text{O}$ values less than -0.10 are probably unique to low temperature sediments (or products of low temperature sediments). The distinction between the different regions outlined here will undoubtedly show more overlap as additional data are collected. Overall, however, the combined $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ values of rocks and waters are characteristic of their formation conditions.

Author Contributions and Acknowledgements

All authors contributed ideas and helped in writing the final manuscript. JW provided unpublished calcite isotope data. We acknowledge E. Cano for unpublished data for mantle samples and two anonymous reviewers.

Editor: Eric H. Oelkers

Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1815>.



This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unrestricted distribution provided the original author and source

are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at <http://www.geochemicalperspectivesletters.org/copyright-and-permissions>.

Cite this letter as: Sharp, Z.D., Wostbrock, J.A.G., Pack, A. (2018) Mass-dependent triple oxygen isotope variations in terrestrial materials. *Geochem. Persp. Let.* 7, 27–31.

References

- CAO, X., LIU, Y. (2011) Equilibrium mass-dependent fractionation relationships for triple oxygen isotopes. *Geochimica et Cosmochimica Acta* 75, 7435–7445.
- CLAYTON, R.N., GROSSMAN, L., MAYEDA, T.K. (1973) A component of primitive nuclear composition in carbonaceous meteorites. *Science* 182, 485–488.
- CRAIG, H. (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochimica et Cosmochimica Acta* 12, 133–149.
- 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., LUZ, B. (2008) Record of $\delta^{18}\text{O}$ and ^{17}O -excess in ice from Vostok Antarctica during the last 150,000 years. *Geophysical Research Letters* 35, doi: 10.1029/2007GL032096.
- LANDAIS, A., RISI, C., BONY, S., VIMEUX, F., DESCROIX, L., FALOURD, S., BOUYGUES, A. (2010) Combined measurements of ^{17}O -excess and d-excess in African monsoon precipitation: Implications for evaluating convective parameterizations. *Earth and Planetary Science Letters* 298, 104–112.
- LI, S., LEVIN, N.E., CHESSON, L.A. (2015) Continental scale variation in ^{17}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.
- MANDERNACK, K.W., FOGEL, M.L., TEBB, B.M., USUL, A. (1995) Oxygen isotope analyses of chemically and microbially produced manganese oxides and manganates. *Geochimica et Cosmochimica Acta* 59, 4409–4425.
- MILLER, M.F. (2002) Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochimica et Cosmochimica Acta* 66, 1881–1889.
- MILLER, M.F. (2018) Precipitation regime influence on oxygen triple-isotope distributions in Antarctic precipitation and ice cores. *Earth and Planetary Science Letters* 481, 316–327.
- 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.
- RISI, C., LANDAIS, A., WINKLER, R., VIMEUX, F. (2013) Can we determine what controls the spatio-temporal distribution of d-excess and ^{17}O -excess in precipitation using the LMDZ general circulation model. *Climate of the Past* 9, 2173–2193.
- SCHOENEMANN, S.W., SCHAUER, A.J., 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}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 SiO_2 - H_2O system and applications to natural samples. *Geochimica et Cosmochimica Acta* 186, 105–119.
- THIEMENS, M.H. (2006) History and application of mass-independent isotope effects. *Annual Review of Earth and Planetary Sciences* 34, 217–262.



■ 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

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

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 α 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 θ_{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 θ value is not constant. It changes with fractionation process (e.g., kinetic, equilibrium) (Matsuhisa *et al.*, 1978; Young *et al.*, 2002). For equilibrium processes, θ 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 δ' (delta-prime) is defined as (Miller, 2002)

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

In δ' notation, θ_{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

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

θ is replaced by λ_{RL} (RL is for reference line) to signify that the best-fit slope is strictly empirical and does not have thermodynamic significance. The γ_{RL} is the y -intercept of the best fit line, often taken as 0‰. With ever-higher precision, λ_{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 λ and γ 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, λ_{RL} is taken as the best-fit slope λ for a set of data in $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ space and γ_{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

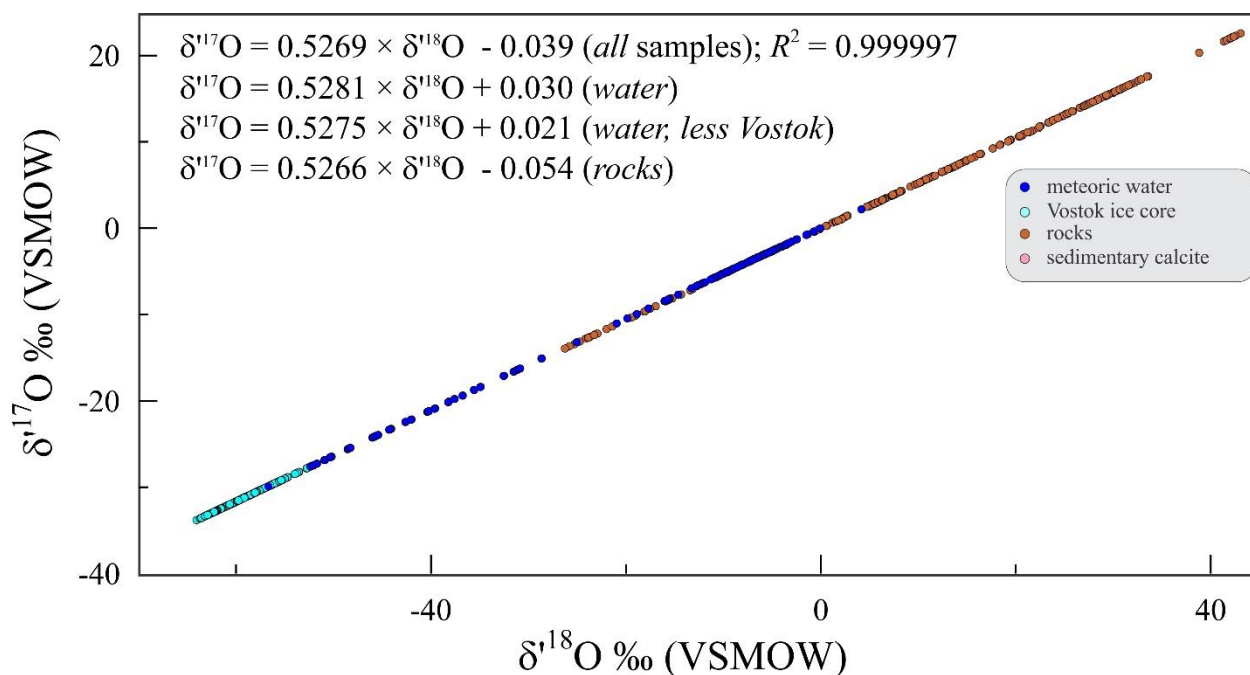


Figure S-1 $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ plot of terrestrial materials (Terrestrial Fractionation Line). All data plot on a line with a slope of 0.5269. The best fit is strongly anchored by the large number of extremely light ice samples from the Vostok core. Excluding these samples, the best-fit line for waters has a slope (λ 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 λ 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.

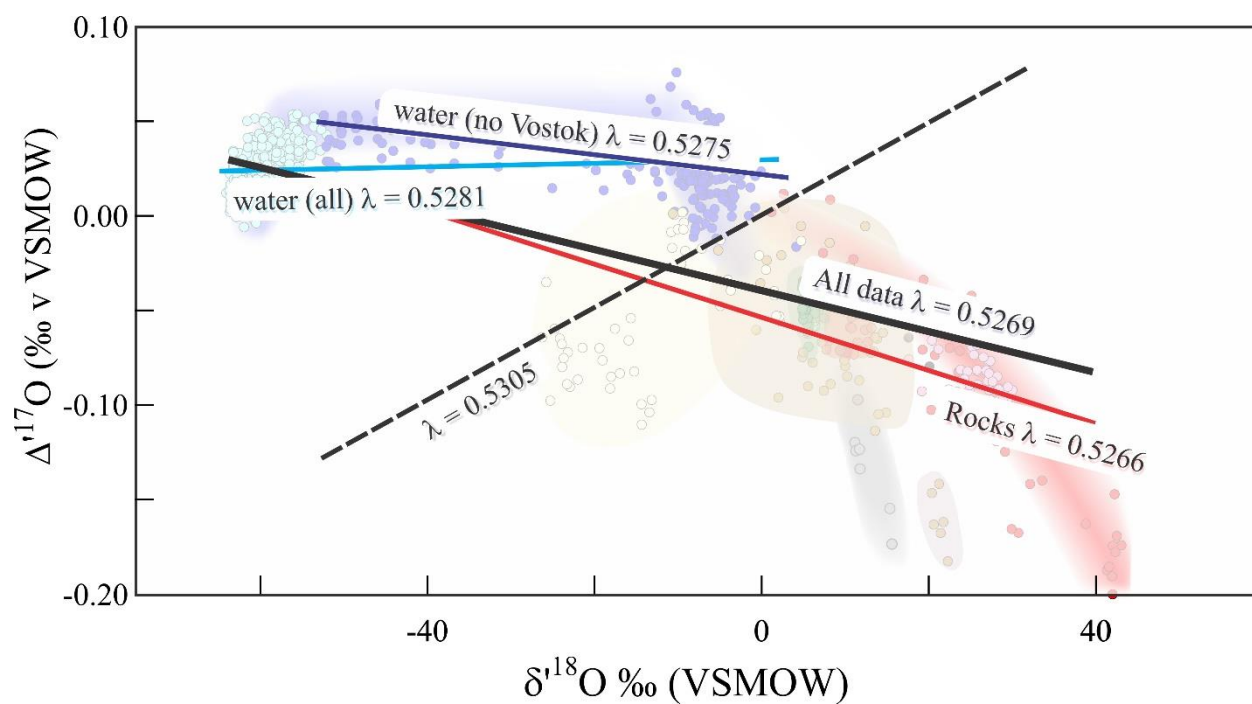


Figure S-2 Plot of the $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ of characteristic materials with various best-fit lines for different materials. All data are fit with a $\lambda = 0.5269$. Waters have a higher λ value while rocks have a lower λ value. The λ value of 0.5305 is the theoretical high-temperature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

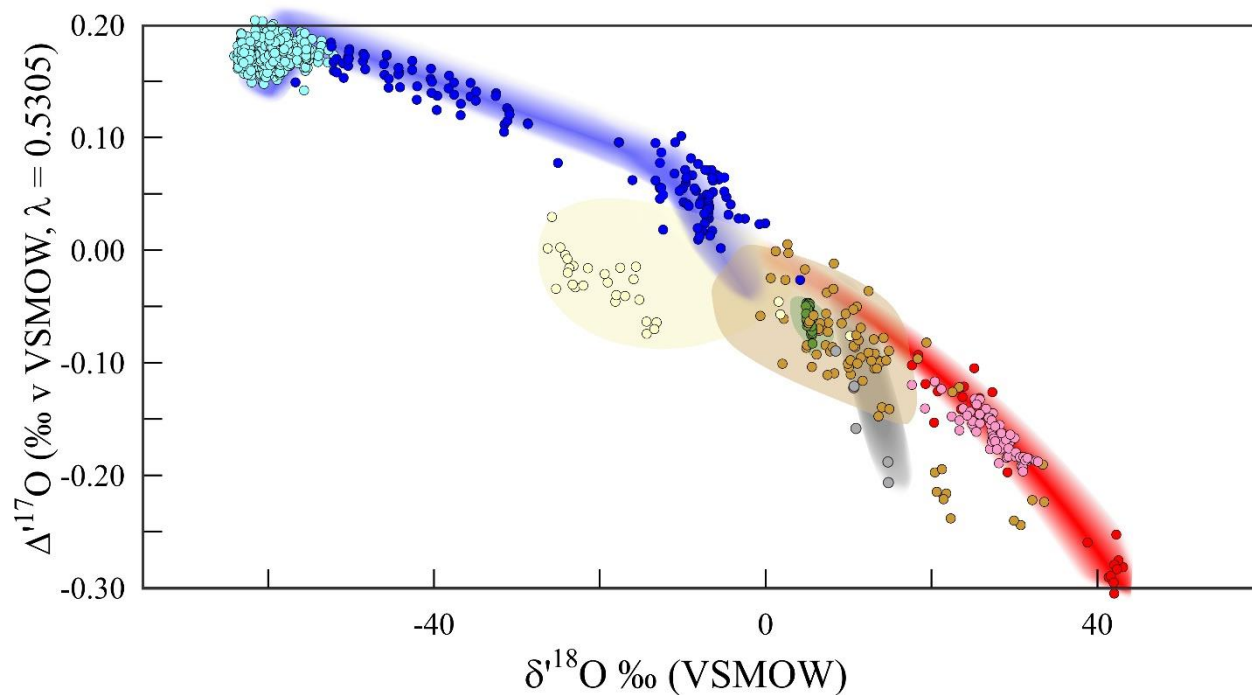


Figure S-3 $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ plot using a $\theta = 0.5305$. The information is identical to that given in Figure 1, but in this plot sample trends have strong negative slopes because the best-fit λ values for natural materials are significantly less than 0.5305. Consequently, 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 λ 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}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}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}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}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. *Geochimica et Cosmochimica Acta* 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}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 SiO_2 - H_2O 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.

