

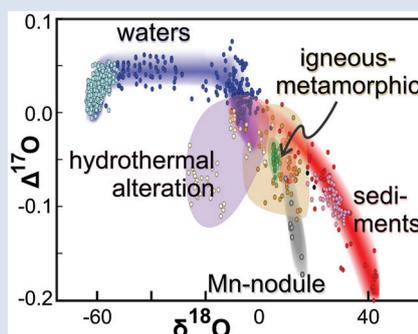
Mass-dependent triple oxygen isotope variations in terrestrial materials

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



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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.

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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 $\sim 1/2$.

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.

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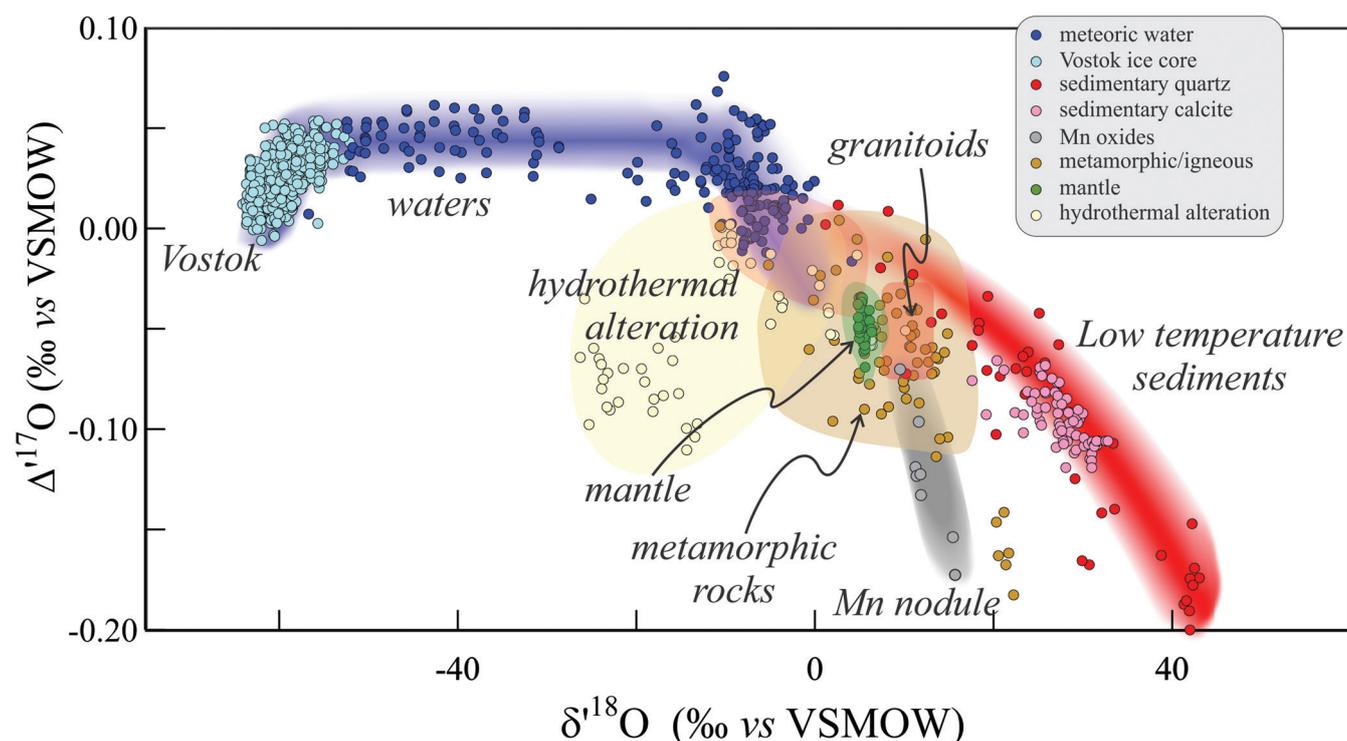


Figure 1 Characteristic $\delta^{18}\text{O}$ – $\Delta^{17}\text{O}$ fields for different materials. Meteoric waters have uniquely high $\Delta^{17}\text{O}$ values and generally low $\delta^{18}\text{O}$ values. Marine carbonates and silica plot in a narrow band of high $\delta^{18}\text{O}$ and low $\Delta^{17}\text{O}$ 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

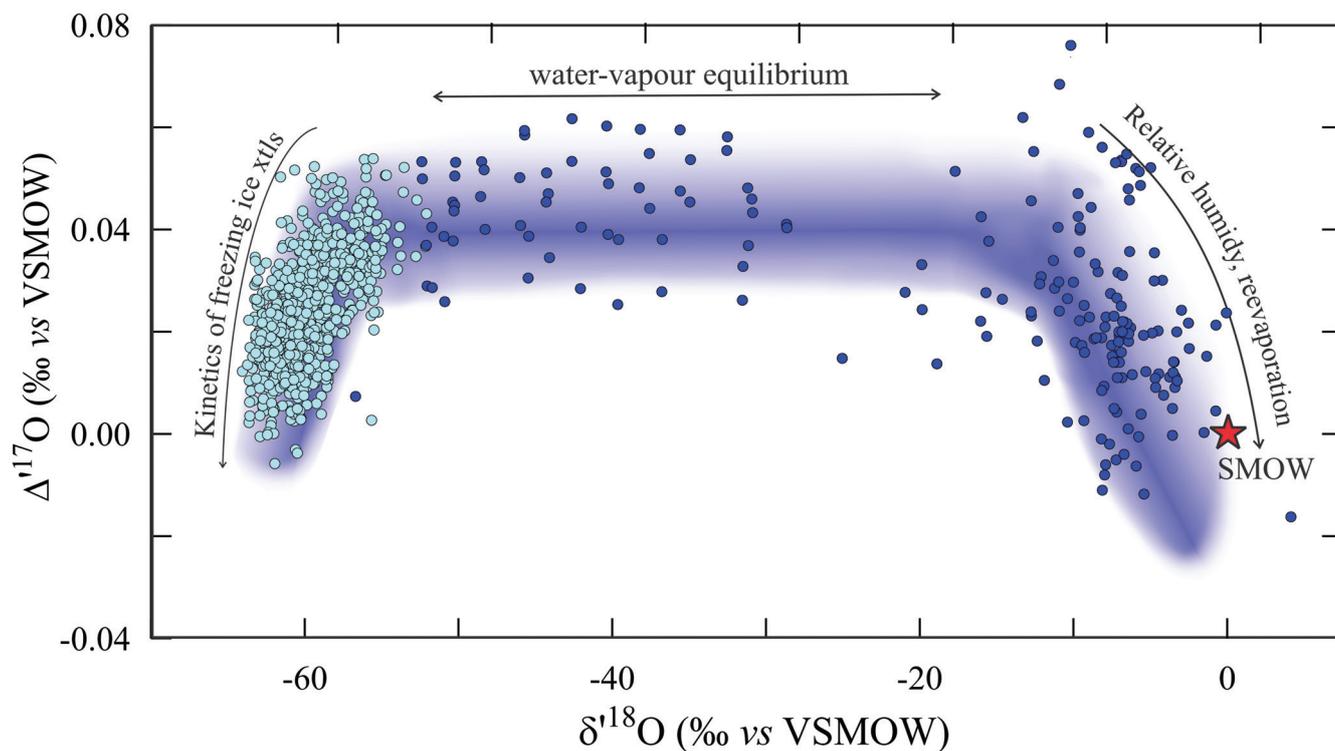


Figure 2 $\delta^{18}\text{O} - \Delta^{17}\text{O}$ values of meteoric waters. Waters can be divided into three segments: extreme low values with a λ of 0.5309 (Vostok ice core - pale blue symbols); light waters with $\delta^{18}\text{O}$ values between -60 and -30 ‰ from high latitudes and a λ of 0.528;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

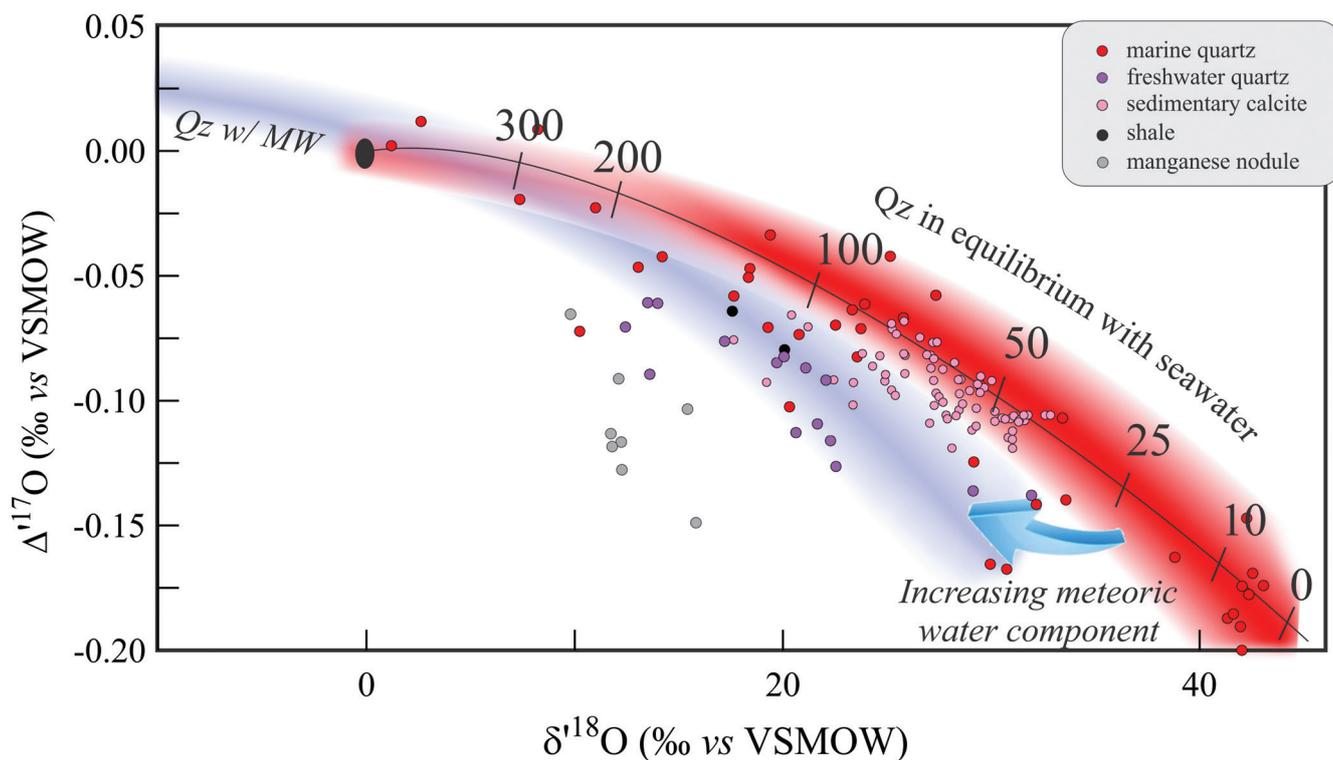


Figure 3 $\delta^{18}\text{O} - \Delta^{17}\text{O}$ plot of sedimentary materials. The red silica samples equilibrated with ocean water plot along the equilibrium fractionation curved line (Sharp *et al.*, 2016) (tick marks indicate equilibrium temperature). Samples equilibrated with meteoric water 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

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

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 granite ($\delta^{18}\text{O} = 8.5 \text{‰}$; $\Delta^{17}\text{O} = -0.05 \text{‰}$) 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 $\delta^{18}\text{O} - \text{low } \Delta^{17}\text{O}$ 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.

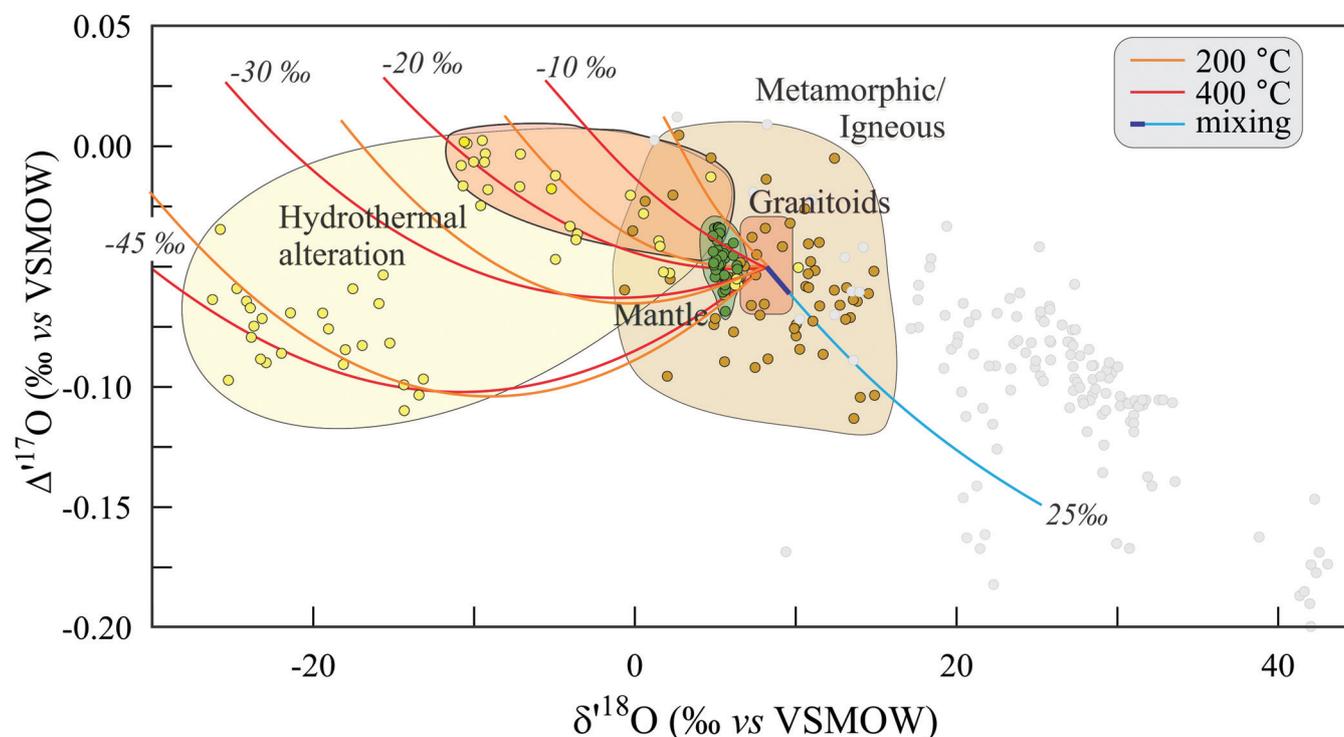


Figure 4 $\delta^{18}\text{O} - \Delta^{17}\text{O}$ values of hydrothermally altered samples (pale yellow field). Calculated alteration paths are shown for a typical granite ($\delta^{18}\text{O} = 8.5 \text{‰}$, $\Delta^{17}\text{O} = -0.05 \text{‰}$) equilibrating with different compositions of meteoric 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 $\Delta^{17}O$ values, whereas meteoric waters generally have positive values. Some studies adopt a $\lambda_{RL} = 0.5305$, 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 $\Delta^{17}O - \delta^{18}O$ 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 $\Delta^{17}O$ as a function of $\delta^{18}O$ in this reference frame (Fig. S-3). The adoption of $\lambda_{RL} = 0.5305$ is consistent with other multiple isotope systems, where the theoretical high-T limit is used as a reference. A $\lambda_{RL} = 0.528$ would make the 'rock' data compatible with the longstanding data on meteoric waters and would not artificially skew $\Delta^{17}O$ to more negative values with increasing $\delta^{18}O$ 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 $\delta^{17}O - \delta^{18}O$ values for all terrestrial materials not affected by photochemical effects plot on a straight line with a slope of $-\frac{1}{2}$. In detail, small, purely mass-dependent variations can be resolved and displayed in $\Delta^{17}O - \delta^{18}O$ space (Fig. 1). The vast majority of meteoric waters have positive $\Delta^{17}O$ values, while rocks have negative $\Delta^{17}O$ 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 $\Delta^{17}O$ 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 $\delta^{18}O - \Delta^{17}O$ values of rocks and waters are characteristic of their formation conditions.

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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.

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Additional Information

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



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