

## ■ Triple oxygen isotopes of meteoric hydrothermal systems – implications for palaeoaltimetry

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### ■ Supplementary Information

The Supplementary Information includes:

- Supplementary Methods
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#### **Supplementary Methods**

Mineral separates were collected by drilling out phenocrysts and then hand picking under a microscope. All samples were measured at Stanford University using a Thermo 253 Plus 10kV IRMS. The laser fluorination method is that established by Sharp (1990) and Sharp *et al.* (2016). In brief, this method involves pre-fluorinating the sample chamber at 30 Torr multiple times to remove any absorbed water before analysis. After no more non-condensables are liberated we lase the individual minerals. For each sample we use a 130 mbar BrF<sub>5</sub> and heat the sample using a CO<sub>2</sub> infrared laser in a vacuumed fluorination line. Only one feldspar separate was loaded per chamber and feldspar samples were always analyzed first in each session. We found that laser times less than 5 minutes produced the most accurate and precise analyses. Following fluorination, the evolved O<sub>2</sub> gas is passed over a heated NaCl trap to remove any F<sub>2</sub> and SiF<sub>4</sub> produced and then frozen onto a 5Å mol sieve. The sample is then frozen onto a second 5Å mol sieve after passing through a He flow through GC column to remove NF<sub>3</sub> and other contaminants. The purified O<sub>2</sub> aliquot is equilibrated within the 253 Plus bellows for 6 minutes and each bellows cycled several times to assure adequate mixing of the gas. Measurements were made for 1.5 to 3+ hours at 5V on mass <sup>32</sup>O<sub>2</sub> to ensure measurement precision of <0.01 ‰ for Δ<sup>17</sup>O. We applied the baseline correction of Yeung *et al.* (2018) and checked this baseline correction about every two weeks. Our reproducibility on sessions where samples from this study are analysed for an internal standard hydrothermal quartz standard L1 is 0.070 ‰ for δ<sup>18</sup>O and 0.016 ‰ for Δ<sup>17</sup>O (n = 23 measurements over 13 months), for UWG-2 (Gore Mountain Garnet) is 0.401 ‰ for δ<sup>18</sup>O and 0.012 ‰ for Δ<sup>17</sup>O (n = 3), and for SCO (San Carlos Olivine, University of New Mexico) is 0.365 ‰ for δ<sup>18</sup>O and 0.005 ‰ for Δ<sup>17</sup>O (n = 5). All of our analyses are relative to published high-precision olivine, garnet and quartz standards; specifically SCO, UWG-2 and L1 values (Pack and Herwartz, 2014; Sharp *et al.*, 2016; Wostbrock *et al.*, 2018, 2020) that were analysed with each batch of samples (Table S-1).

## Supplementary Equations

Stable isotope fractionation between two substances (a and b) is described by the basic equation:

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

In this equation R is the ratio of the heavy to light isotope. Here  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$ . The delta notation is:

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

Rearranging equations S-1 and S-2 the alpha value can be expressed as:

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

The alpha values for oxygen 17 and 18 are related by their exponent  $\theta$ , as such:

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

$\theta$  varies as a function of equilibrium and kinetic processes (Young *et al.*, 2002) and for equilibrium process it is temperature dependent (Sharp *et al.*, 2016).

Equation S-4 in linear form is:

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

The linearised values of  $\delta$  values given by:

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

The  $\theta$  value for the linearised  $\delta'$  value is given as:

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

For triple oxygen isotope analysis we use the deviation of isotope values from the terrestrial isotope fractionation line, which has a slope of  $\sim 1/2$  in  $\delta^{18}\text{O}$  vs.  $\delta^{17}\text{O}$  space. The terrestrial fractionation line is defined as:

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

You will note here that  $\theta$  has been replaced by  $\lambda$  to emphasize the difference between process-based values ( $\theta$ ) and empirical values ( $\lambda$ ). The subscript RL refers to the reference line used (see following). The Y intercept of this equation is  $\gamma$ , which is taken as zero. One of the difficulties introduced into comparing triple oxygen results is the selection of which  $\lambda$  to use as these vary between different substances and different processes. Following Sharp *et al.* (2018) we use a value of 0.528 ( $\lambda$ ) in equation S-9.

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

For individual hand sample mineral pairs (quartz-feldspar) we calculate apparent  $\lambda_{\text{quartz-feldspar}}$  values following equation S7. We denote this using  $\lambda$  as this slope may represent mixing or non-equilibrium (*i.e.* kinetically controlled) processes during fluid-rock interaction, whereby the plagioclase is more exchanged than the quartz.

To calculate the end-member alteration waters (*i.e.* hydrothermal waters derived from meteoric waters at infinite fluid/rock interaction) we modify the approach of Herwartz *et al.* (2015) (see also Zakharov *et al.*, 2017) using equations originally presented by Taylor (1978). Using a simple mass-balance mixing model, the fraction of water (X) allowed to equilibrate with a rock at a given temperature gives the bulk composition by the equations (where  $\delta^*\text{O}$  is for  $\delta^{17}\text{O}$  or  $\delta^{18}\text{O}$ ):

$$\delta^*\text{O}_{\text{bulk}} = X_{\text{water}} (\delta^*\text{O}_{\text{water,initial}}) + (1-X_{\text{water}}) (\delta^*\text{O}_{\text{rock,initial}}) \quad \text{Eq. S-10}$$

$$\delta^*\text{O}_{\text{bulk}} = X_{\text{water}} (\delta^*\text{O}_{\text{water,final}}) + (1-X_{\text{water}}) (\delta^*\text{O}_{\text{rock,final}}) \quad \text{Eq. S-11}$$



$\delta^x\text{O}$  can be either  $\delta^{18}\text{O}$  or  $\delta^{17}\text{O}$ . The final  $\delta^x\text{O}$  value of the rock is determined by the additional equation:

$$\alpha^x = \frac{1000 + \delta^x\text{O}_{\text{final rock}}}{1000 + \delta^x\text{O}_{\text{final water}}} \quad \text{Eq. S-12}$$

This leads to the relationship between the initial rock and water oxygen isotope compositions, the fluid/rock ratio and the final isotopic composition of the rock:

$$\delta^x\text{O}_{\text{rock final}} = \frac{1000X + \alpha(X \cdot \delta^x\text{O}_{\text{rock initial}} - X \cdot \delta^x\text{O}_{\text{water initial}} - \delta^x\text{O}_{\text{rock initial}} - 1000X)}{\alpha X - \alpha - X} \quad \text{Eq. S-13}$$

In order to calculate the alteration relationship of the feldspar minerals analysed in this study we use apply the fractionation factor of Matsuhisa *et al.* (1979) assuming the feldspar (plagioclase) analysed here is 20 % Anorthite and 80 % Albite, and the following equations for triple oxygen isotopes to derive the end-members. The equilibrium fractionation for  $\delta^{18}\text{O}$  between a mineral and water is given by:

$$\delta^{18}\text{O}_{\text{mineral}} = \delta^{18}\text{O}_{\text{water}} + \frac{a \times 10^6}{T^2} + \frac{b \times 10^3}{T} + c \quad \text{Eq. S-14}$$

where a, b and c are fitted or theoretically derived coefficients (note that b=0 in Matsuhisa *et al.* (1979); a = 2.21 and c = -2.57). Which, given the relationships described above the equilibrium fractionation for  $\delta^{17}\text{O}$  and  $\Delta^{17}\text{O}$ , where  $\epsilon$  is fitted slope for the temperature dependence of  $\theta$ ; e.g., Sharp *et al.*, 2016), is thus:

$$\delta^{17}\text{O}_{\text{mineral}} = \delta^{17}\text{O}_{\text{water}} + \left( \frac{a \times 10^6}{T^2} + \frac{b \times 10^3}{T} + c \right) \left( 0.5305 - \frac{\epsilon}{T} \right) \quad \text{Eq. S-15}$$

$$\Delta^{17}\text{O}_{\text{mineral}} = \delta^{17}\text{O}_{\text{water}} - \lambda \cdot \delta^{18}\text{O}_{\text{water}} + \left( \frac{a \times 10^6}{T^2} + \frac{b \times 10^3}{T} + c \right) \left( 0.5305 - \frac{\epsilon}{T} - \lambda \right) \quad \text{Eq. S-16}$$

The fitted slope dependence ( $\epsilon$ ) is set here to 1.7 (quartz-water is 1.85; Sharp *et al.*, 2016; Wostbrock *et al.*, 2018) based on lower  $\delta^{18}\text{O}$  fractionation factors (at equivalent temperatures) for feldspar, although no experimental or natural datasets yet exist to assess this value. We note that our calculations are insensitive to  $\epsilon$  values ranging from 1.5 to 1.85. Then, combining the equation S-14 and S-16, a relationship between the  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for a mineral in equilibrium with water is thus:

$$\Delta^{17}\text{O} = \delta^{17}\text{O}_w + (\delta^{18}\text{O}_r - \delta^{18}\text{O}_w) \left( 0.5305 + \frac{(c - \delta^{18}\text{O}_r + \delta^{18}\text{O}_w)\epsilon}{500(b + \sqrt{b^2 - 4a(c - \delta^{18}\text{O}_r + \delta^{18}\text{O}_w)})} - \lambda \right) - \delta^{18}\text{O}_w \cdot \lambda \quad \text{Eq. S-17}$$

Finally, by assuming an end-member initial feldspar values ( $\Delta^{17}\text{O} = -0.082$  and  $\delta^{18}\text{O} = 8.78$ ) based on our data and temperature (400 °C based on Criss and Taylor, 1983), we derive a best fit to the  $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$  array of feldspar data (black line on Fig. 3) for equation S-13 (using equation S-17) for fractional mixing (X) of 0 (rock-buffered end-member) to 1 (water-buffered end-member, i.e., fluid/rock of infinity). The best fit (determined via lowest RMSE) and uncertainty on the best fit to this array was assessed using the measurement error (Table S-1) and error on the end-member initial feldspar values via a Monte Carlo routine. Sensitivity to the choice of alteration temperature is shown in Figure S-1 *via* the equation that follows from the above relationships as (excluding b for our purposes, see above):

$$\delta^{18}\text{O}_{\text{water}} = \delta^{18}\text{O}_{\text{rock}} - c - \frac{a \times 10^6}{T^2} \quad \text{Eq. S-18}$$

Where we approximate the rock  $\delta^{18}\text{O}$  to that of the end-member derived from the triple oxygen isotope relationship in Figure 3 ( $\delta^{18}\text{O}_{\text{rock,final}} = -9.68$  when X=1). The associated end-member meteoric water uncertainty extrapolated to the meteoric water line of Passey and Ji (2019) is given in Table S-2 and on Figure 3; however, full inclusion of the meteoric water line uncertainty (dashed lines in Figure 3 from Passey and Ji (2019), chosen because those data (grey diamonds on Figure 3) are from western North America) dominate the uncertainty associated with these calculations (range given in main text). Calculations using assumptions of different meteoric water line slopes and intercepts are given in Table S-2 to demonstrate the range of differences given our current knowledge of the meteoric water line.



## Supplementary Tables

**Table S-1** Triple oxygen isotope and D/H measurements of Idaho Batholite samples. Standards averaged only over sessions when data was produced (December 2018 to December 2019). All oxygen isotope data is normalized to SCO, UWG-2 and L1 values in Wostbrock *et al.* (2020). Biotite  $\delta D$  were measured in triplicate. All values versus VSMOW.

Feldspar Measurements							
Sample ID	Hand Sample No	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	$\Delta^{17}O (\lambda = 0.528)$	$\Delta^{17}O$ Meas. SE
ID-18-01	1	-0.154	-0.204	-0.154	-0.204	-0.046	0.007
ID-18-02	2	1.523	3.043	1.524	3.048	-0.084	0.007
ID-18-03	3	4.480	8.623	4.490	8.661	-0.074	0.007
ID-18-04a	4						
ID-18-04b	4	4.541	8.781	4.551	8.819	-0.095	0.008
ID-18-05	5	2.997	5.769	3.001	5.786	-0.049	0.008
ID-18-06	6	4.085	7.897	4.094	7.929	-0.085	0.007
ID-18-07a	7	-1.883	-3.532	-1.881	-3.526	-0.018	0.008
ID-18-07b	7						
ID-18-08a	8	-1.897	-3.587	-1.896	-3.580	-0.004	0.008
ID-18-08b	8	4.044	7.803	4.052	7.833	-0.076	0.009
ID-18-09	9	0.529	1.061	0.530	1.061	-0.031	0.006
ID-18-10	10	1.947	3.827	1.949	3.834	-0.073	0.008
ID-18-11	11	2.404	4.655	2.406	4.666	-0.054	0.006
ID-18-12	12	0.556	1.200	0.556	1.201	-0.078	0.008
Quartz Measurements							
Sample ID	$\delta^{17}O$	$\delta^{18}O$	$\delta^{17}O$	$\delta^{18}O$	$\Delta^{17}O (\lambda = 0.528)$	$\Delta^{17}O$ Meas. SE	$\lambda_{\text{quartz-feldspar}}$
ID-18-01	2.778	5.485	2.782	5.500	-0.118	0.009	0.51529
ID-18-02	4.697	9.059	4.709	9.101	-0.086	0.009	0.52764
ID-18-03	4.929	9.480	4.942	9.525	-0.076	0.006	0.52523
ID-18-04a							
ID-18-04b							
ID-18-05	5.430	10.491	5.444	10.547	-0.110	0.008	0.51522
ID-18-06	5.280	10.152	5.294	10.203	-0.080	0.008	0.52986
ID-18-07a	5.509	10.619	5.524	10.675	-0.098	0.008	0.52239
ID-18-07b	5.219	10.008	5.232	10.058	-0.065	0.008	0.52147
ID-18-08a							
ID-18-08b							
ID-18-09	4.024	7.730	4.032	7.760	-0.058	0.007	0.52393
ID-18-10	4.386	8.425	4.396	8.460	-0.062	0.007	0.53053
ID-18-11							
ID-18-12	4.389	8.495	4.399	8.531	-0.097	0.008	0.52543
Standards							
Standard ID	No.	$\delta^{17}O$	$\delta^{18}O$	$\delta^{18}O$	$\delta^{18}O$ SD	$\Delta^{17}O (\lambda = 0.528)$	$\Delta^{17}O$ SD
UWG-2	3	3.064	5.910	5.927	0.401	-0.056	0.012
SCO (UNM)	5	2.687	5.189	5.203	0.365	-0.053	0.005
L1 (UNM)	23	9.270	17.735	17.893	0.070	-0.094	0.016
Comparison to Wostbrock et al. (2020) Values							
Standard ID	$\delta^{18}O$	$\delta^{18}O$ SD	$\Delta^{17}O (\lambda = 0.528)$	$\delta^{18}O$ SD	$\delta^{18}O$ Difference	$\Delta^{17}O$ Difference	
UWG-2	5.696	0.115	-0.071	0.005	-0.231	-0.015	
SCO (UNM)	5.268	0.096	-0.058	0.005	0.065	-0.005	
L1 (UNM)	18.07	0.136	-0.081	0.005	0.177	0.013	
Biotite Measurements							
Sample ID	$\delta D$	$\delta D$ Rep. SE					
ID-18-01	-139.9	0.9					
ID-18-02	-137.3	4.7					
ID-18-03	-106.4	7.3					
ID-18-04a	-148.9	3.5					



ID-18-04b	-138.2	2.6
ID-18-05	-142.5	1.3
ID-18-06	-129.5	1.1
ID-18-07a	-144.8	2.6
ID-18-07b		
ID-18-08a	-145.7	0.8
ID-18-08b	-145.7	0.8
ID-18-09	-148.5	1.3
ID-18-10	-151.8	1.3
ID-18-11		
ID-18-12	-148.1	3.9

**Table S-2** Meteoric Water Line Assumption and Calculated Idaho Batholith Meteoric Waters

Reference	Slope	Intercept	$\delta^{18}\text{O}_{\text{mw}}$	$\Delta^{17}\text{O} (\lambda = 0.528)$	$\delta^{17}\text{O}_{\text{mw}}$	$\delta^{18}\text{O}_{\text{mw}}$	$\delta^{18}\text{O}_{\text{mw}}$ SD	$\Delta\delta^{18}\text{O}$ <sup>3</sup>	Elevation (km) <sup>4</sup>	SD plus	SD minus	Note
Passey and Ji (2019)	0.528	0.032	-11.920	0.032	-6.320	-11.992	1.106	-5.920	3.11	0.312	-0.377	1, 5
Sharp et al. (2018)	0.52654	0.014	-12.378	0.008	-6.590	-12.455	1.480	-6.378	3.34	0.474	-0.386	2
Luz and Barkan (2010)	0.528	0.037	-12.615	0.037	-6.688	-12.695	1.209	-6.615	3.56	0.544	-0.407	5
Herwartz et al. (2015)	0.5285	0.03	-11.383	0.024	-6.039	-11.448	1.220	-5.383	2.87	0.297	-0.363	
							<b><math>\delta\text{D}</math>-based Estimate</b>	-10.000	4.74	0.637	-0.487	6

**Notes**

1 Based on western United States waters that include data in Li *et al.* (2016)

2 Equation as given in text of Sharp *et al.* (2018)

3 Assuming a  $\delta^{18}\text{O}$  a coastal value of -6 (Mulch *et al.*, 2006; Mix *et al.*, 2016; Feng *et al.*, 2013; Methner *et al.*, 2016)

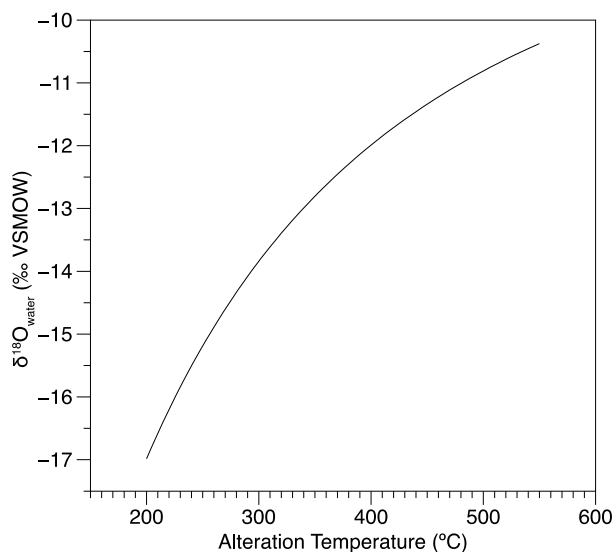
4 Based on propagation through Rowley *et al.* (2001) model

5 By definition, in the  $\lambda = 0.528$  reference frame, because the slope is 0.528 the  $\Delta^{17}\text{O}$  must be equal to the intercept of the MWL.

6 Approximate value for Criss and Taylor (1983) and McFadden *et al.* (2015)



## Supplementary Figures



**Figure S-1** Sensitivity of calculations to different alteration temperatures via equation S18 using the plagioclase water fractionation factor of Matsuhisa *et al.* (1979) and our derived rock-end-member ( $\delta^{18}\text{O}_{\text{rock,final}} = -9.68$ , assuming an alteration temperature of 400 °C). Assuming a range of temperatures (*e.g.*, 250 to 500 °C) does not influence the assumed  $\delta^{18}\text{O}_{\text{rock,final}}$  fitted value (*e.g.*, Figure 3) by more than ~0.3 ‰, though it does require lower (higher)  $\delta^{18}\text{O}_{\text{water,final}}$  values for lower (higher) temperatures.

## Supplementary Information References

- Feng, R., Poulsen, C.J., Werner, M., Chamberlain, C.P., Mix, Hari T., Mulch, A. (2013) Evolution of Early Cenozoic topography, climate and stable isotopes of precipitation in the North America Cordillera. *American Journal of Science* 313, 613-648.
- Li, S., Levin, N.E., Chesson, L.A. (2015). Continental scale variation in 17O-excess of meteoric waters in the United States. *Geochimica et Cosmochimica Acta* 164, 110-126.
- Luz, B., Barkan, E. (2010). Variations of 17O/16O and 18O/16O in meteoric waters. *Geochimica et Cosmochimica Acta* 74, 6276-6286.
- Matsuhisa, Y., Goldsmith, J.R., Clayton, R.N. (1979). Oxygen isotopic fractionation in the system quartz-albite-anorthite-water. *Geochimica et Cosmochimica Acta* 43, 1131-1140.
- Methner, K., Feibig, J., Umhoefer, P., Chamberlain, P., Mulch, A. (2016) Eo-Oligocene proto-Cascades topography revealed by clumped ( $\Delta 47$ ) and oxygen isotope ( $\delta 18\text{O}$ ) geochemistry (Chumstick Basin, WA, USA). *Tectonics* 35, 546-564. doi:10.1002/2015TCC003984
- Mix, H., Ibarra, D., Mulch, A., Graham, S., Chamberlain, C.P. (2016) A hot and high Eocene Sierra Nevada. *Geological Society of America Bulletin* 16, 531-542. doi:10.1130/B31294.1
- Passey, B.H., Ji, H. (2019). Triple oxygen isotope signatures of evaporation in lake waters and carbonates: A case study from the western United States. *Earth and Planetary Science Letters* 518, 1-12.
- Pack, A., Herwartz, D. (2014) The triple oxygen isotope composition of the Earth mantle and understanding  $\Delta 17\text{O}$  variations in terrestrial rocks and minerals. *Earth and Planetary Science Letters* 390, 138-145. doi.org/10.1016/j.epsl.2014.01.017.
- Sharp, Z.D. (1990) A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides. *Geochimica et Cosmochimica Acta* 54, 1353-1357.
- 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<sub>2</sub>-H<sub>2</sub>O system and applications to natural samples. *Geochimica et Cosmochimica Acta* 186, 105-119.
- Sharp, Z.D., Wostbrock, J.A.G., Pack, A. (2018) Mass-dependent triple oxygen isotope variations in terrestrial materials. *Geochemical Perspectives Letters* 7, 27-31.
- Taylor, H.P., Jr. (1978) Oxygen and hydrogen isotope systematics of plutonic granitic rocks. *Earth and Planetary Science Letters* 38, 177-210.
- Wostbrock, J.A.G., Sharp, Z.D., Sanchez-Young, C., Reich, M., van den Heuvel, D.B., Benning, L.G. (2018) Calibration and application of silica-water triple oxygen isotope thermometry to geothermal systems in Iceland and Chile. *Geochimica et Cosmochimica Acta* 234, 84-97.
- Wostbrock, J.A.G., Cano, E.J., Sharp, Z.D. (2020) An internally consistent triple oxygen isotope calibration of standards for silicates, carbonates and air relative to VSMOW2 and SLAP2. *Chemical Geology* 533, 119432.
- Yeung, L.Y., Hayles, J.A., Hu, H., Ash, J.L., Sun, T. (2018) Scale distortion from pressure baselines as a source of inaccuracy in triple-isotope measurements. *Rapid Communications in Mass Spectrometry* 32, 1811-1821.
- 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.

