

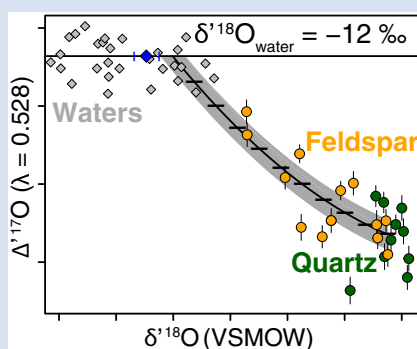
## Triple oxygen isotopes of meteoric hydrothermal systems – implications for palaeoaltimetry

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### Abstract



We use triple oxygen isotopes of altered granitic rocks to determine the isotope composition of meteoric waters in a fossil hydrothermal system, the low  $\delta^{18}\text{O}$  Eocene Idaho Batholith, originally studied by [Criss and Taylor \(1983\)](#). In doing so we: 1) test whether meteoric water values estimated from previous  $\delta^{18}\text{O}$  and  $\delta\text{D}$  analyses on quartz, feldspar and biotite are robust and 2) determine the palaeoelevation of the Eocene highlands that are presently constrained primarily by the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of paired muscovite and quartz from core complexes and altered granites.

Our calculated  $\delta^{18}\text{O}$  values of meteoric water are higher than estimates that use combined feldspar  $\delta^{18}\text{O}$  and biotite  $\delta\text{D}$  measurements in these hydrothermally altered granites and  $\delta\text{D}$  values from muscovite from nearby core complexes ([Mulch \*et al.\*, 2004](#)). Both methods are consistent with a high elevation ( $\sim 3.1$  to  $4.7$  km) Eocene highland in the northwestern U.S. Cordillera.

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### Introduction

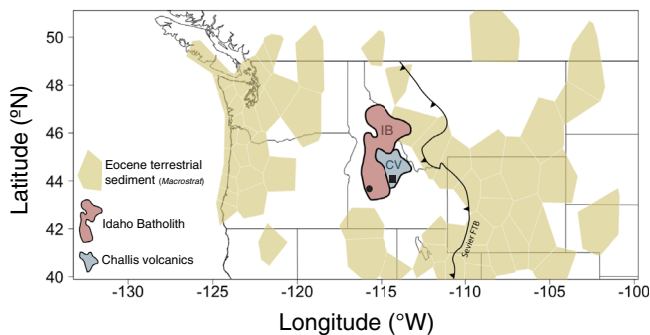
With the advent of stable isotope palaeoaltimetry it has been possible to determine the past elevations of the world's major mountain belts by exploiting the relationship between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of meteoric waters and elevation as described by Rayleigh distillation over orography ([Poage and Chamberlain, 2001](#); [Rowley \*et al.\*, 2001](#)). Multiple proxies for the isotopic composition of meteoric waters have been used for these elevation reconstructions. These include the  $\delta\text{D}$  of 1) organic molecules from fossilised leaves ([Hren \*et al.\*, 2010](#)), hydrated volcanic glasses ([Mulch \*et al.\*, 2008](#)), pedogenic clays ([Chamberlain \*et al.\*, 1999](#)), hydrothermal micas ([Mulch \*et al.\*, 2004](#)), fluid inclusions of quartz veins ([Sharp \*et al.\*, 2005](#)); and the  $\delta^{18}\text{O}$  of 2) pedogenic and lacustrine carbonate ([Quade \*et al.\*, 2007](#)), lacustrine chert ([Davis \*et al.\*, 2009](#)), and pedogenic clays ([Mix and Chamberlain, 2014](#)). While these proxies are excellent predictors of the isotopic composition of meteoric waters they are limited by their geographic location as many occur only in the sedimentary basins that flank the crystalline cores of mountain belts. Nowhere is this more prevalent than in the North American Cordillera where almost all palaeoelevation estimates come from intermontane basins that are adjacent to crystalline uplifts ([Chamberlain \*et al.\*, 2012](#); [Fig. 1](#)).

Most determinations of the isotopic composition of meteoric waters using crystalline rocks rely on the  $\delta\text{D}$  of micas from hydrothermally altered rocks within fault zones ([Mulch \*et al.\*, 2004](#)) or altered granites ([Criss and Taylor, 1983](#)). A potential problem with this approach is that hydrogen isotopes of phyllosilicates may continue to exchange well after crystallisation. For example, [O'Neil and Kharaka \(1976\)](#) showed that exchange of hydrogen, but not oxygen, occurred in clay minerals at temperatures above  $100^\circ\text{C}$ . It is also possible that micas may be exchanging H rather than OH groups and that this exchange occurs at temperatures typical of cooling crystalline rocks. If this is the case, then the oxygen and hydrogen isotope values of micas may be decoupled and cooling rate dependent ([Graham \*et al.\*, 1987](#)). Hence, the motivation of this study is to use triple oxygen isotopes to determine the isotopic composition of meteoric waters. Unlike the H-O system, the  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  systems are not decoupled, and should change in concert during alteration.

To estimate the isotopic composition of meteoric water in a hydrothermal system, we modify the approach of [Herwartz \*et al.\* \(2015\)](#) who used arrays of triple oxygen isotopes on a suite of rocks to determine the  $\delta^{18}\text{O}$  of alteration waters during a Snowball Earth event (see also [Zakharov \*et al.\*, 2017](#)). Here, we use mixing equations ([Taylor, 1978](#)) modified for  $^{17}\text{O}$  to

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**Figure 1** Map of Idaho batholith and surrounding Eocene basins. Symbols represent the study area (dot), and the Pioneer core complex (square).

determine the palaeoelevation of Eocene hydrothermally altered rocks of the Idaho batholith (Criss and Taylor, 1983). We show that triple oxygen isotopes correspond to Eocene meteoric water values that are higher than those determined by hydrogen isotope analysis, suggesting that retrograde hydrogen, but not oxygen, isotope exchange has occurred between micas and fluids.

## Geologic Setting

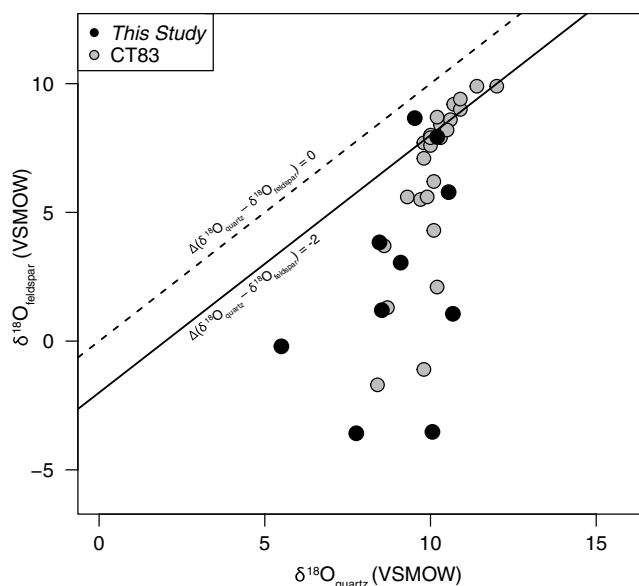
The Idaho batholith (~25 000 km<sup>2</sup>) lies within the crystalline core of the North American Cordillera. It is flanked on both the west and east by Cenozoic intermontane basins that contain debris eroded from the batholith and surrounding rocks (Fig. 1). The batholith is Cretaceous to Eocene in age and consists of granites and granodiorites (Gaschnig *et al.*, 2010). The batholith was hydrothermally altered during the emplacement of the Eocene plutons and eruption of the Challis volcanics. Using hydrogen and oxygen isotopes of minerals from these Eocene granites, Criss and Taylor (1983) demonstrated that the hydrothermal systems consisted of meteoric waters within flow systems centred on the Eocene plutons. The hydrothermal centre targeted here, the Rocky Bar complex, lies in the southwest corner of the Idaho Batholith.

The Rocky Bar complex was emplaced (~48 Ma; Gaschnig *et al.*, 2010) and hydrothermally altered (~45 to 37 Ma; Criss *et al.*, 1982) during the Eocene. The alteration of the pluton and wall-rocks is evidenced by low  $\delta^{18}\text{O}$  values of plagioclase (down to -2.5 ‰), with the lowest values occurring near the core of the pluton and along the faults that ring the complex. Guided by the results of Criss and Taylor (1983), we collected granites from the Rocky Bar complex exposed along Highway 21 that transects the complex (Table S-1).

## Results

Our analysis of  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$  of plagioclase and quartz, and  $\delta\text{D}$  of biotite give three results, which are:

First, the  $\delta^{18}\text{O}$  of plagioclase has larger variations than that of quartz. The  $\delta^{18}\text{O}$  of plagioclase ranges from -3.6 to 8.8 ‰; quartz  $\delta^{18}\text{O}$  values range from 5.5 to 10.7 ‰ (Table S-1). Moreover, the  $\delta^{18}\text{O}$  of coexisting mineral pairs form disequilibrium arrays (Fig. 2) similar to those discovered by Criss and Taylor (1983). Second, the  $\Delta^{17}\text{O}$  ( $\delta^{17}\text{O} - 0.528 \times \delta^{18}\text{O}$ ) of plagioclase, like the  $\delta^{18}\text{O}$  values, show a wider range than that of quartz.  $\Delta^{17}\text{O}$  of plagioclase ranges from -0.004 to -0.095, and  $\Delta^{17}\text{O}$  of quartz ranges from -0.058 to -0.118. Third, the  $\delta^{18}\text{O}$  of feldspar and  $\delta\text{D}$  values of biotite also form a water-rock mixing array (Fig. 4, Table S-1).



**Figure 2**  $\delta^{18}\text{O}_{\text{quartz}}$  versus  $\delta^{18}\text{O}_{\text{plagioclase}}$  for coexisting mineral pairs. Black dots are this study and gray dots those of Criss and Taylor (1983). Shown are the  $\Delta_{\text{qtz-plag}}$  for 0 and 2.0 ‰. 2.0 ‰ is the equilibrium fractionation between quartz and feldspar for granitic rocks (O'Neil and Taylor, 1967).

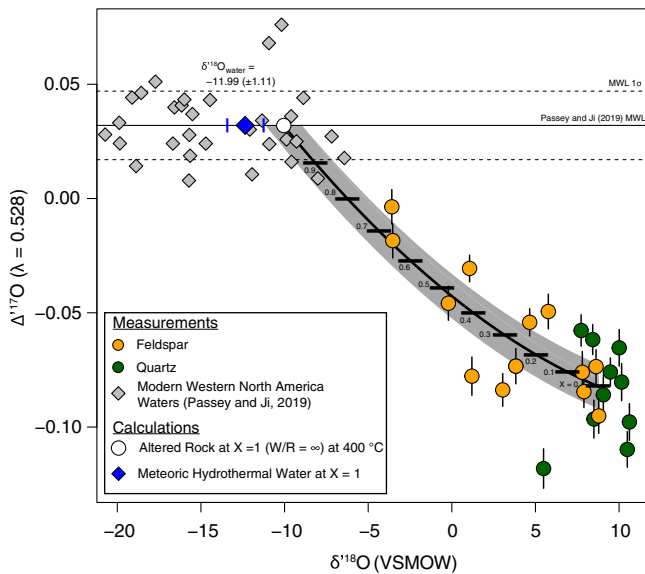
## Interpretation

Our results agree with the interpretation that the oxygen and hydrogen isotopes reflect a high temperature hydrothermal system during emplacement of the Eocene plutons (Criss and Taylor, 1983). Disequilibrium arrays of the oxygen isotopes of paired quartz and plagioclase (Fig. 2) result from differential exchange between fluids and quartz/feldspar during hydrothermal activity, with feldspar exchanging more rapidly than quartz. These kinetic controls are also reflected in the  $\Delta^{17}\text{O}$  values.

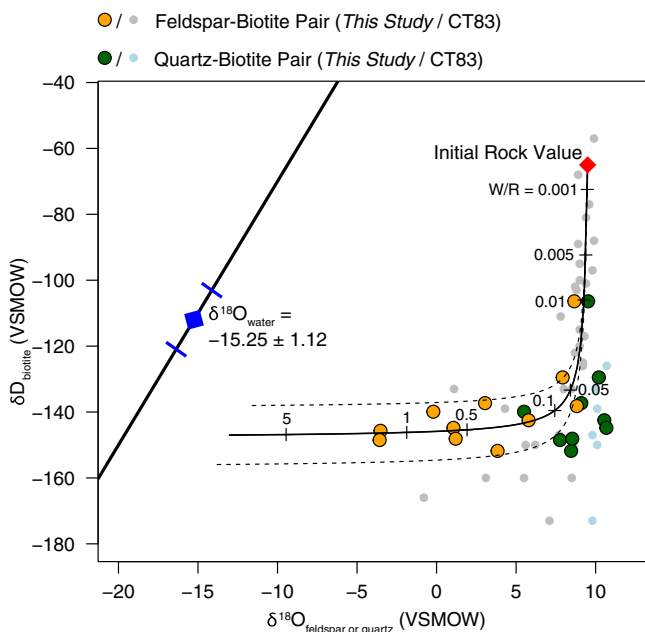
The kinetic effects are evidenced by the wide range of  $\lambda_{\text{quartz-feldspar}}$  values. Note that, following Pack and Herwartz (2014) and Sharp *et al.* (2018), we use  $\theta$  to represent the theoretical slope, whereas  $\lambda$  is used to represent the empirical slope using data. As stated above our  $\lambda_{\text{quartz-feldspar}}$  values range from 0.5152 to 0.5305 (Table S-1). The theoretical high temperature slope is  $\theta = 0.5305$  (Young *et al.*, 2002). Given the wide range of  $\lambda_{\text{quartz-feldspar}}$  values (Table S-1) and the narrow temperature range experienced by these granites and high temperature fluids it is highly unlikely that these minerals are in isotopic equilibrium. Thus, our results are consistent with the interpretation of Criss and Taylor (1983), but with the added constraint that we can calculate the meteoric water composition using oxygen isotopes alone.

To determine the oxygen isotopic composition of meteoric water we used the array of  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  (Fig. 3) values for plagioclase. A fit through this array (see Supplementary Information) using the water-rock equations of Taylor (1978) assuming a 400 °C alteration temperature, gives a value of  $\delta^{18}\text{O}$  of meteoric water of -11.99 ‰ ( $\pm 1.11$ ,  $1\sigma$ ). Propagating the uncertainty around the meteoric water line of Passey and Ji (2019) (dashed lines in Fig. 3) and the best fit regression shown in Figure 3, produces a field spanning -10 to -15 ‰ (see Table S-2). Additionally, if the feldspar-H<sub>2</sub>O interaction is set to a colder temperature, such as 250 °C, rather than the maximum 400 °C assumed by Criss and Taylor (1983), we calculate a  $\delta^{18}\text{O}$  of meteoric water of -15 ‰ (Fig. S-1). However, this lower temperature is probably unreasonable given that it is below the closure temperature of the dated hydrothermal micas

(Criss and Taylor, 1983). Regardless, it is clear that the Eocene meteoric water has a low  $\delta^{18}\text{O}$  value. However, our  $\delta^{18}\text{O}$  value is higher than that determined previously (approximately  $-16\text{‰}$ ) by Criss and Taylor (1983) who use both  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values. Our  $\delta^{18}\text{O}$ - $\delta\text{D}$  data give results similar to Criss and Taylor (1983) with a best fit to the data of  $\delta^{18}\text{O} = -15.25\text{‰}$  ( $\pm 1.12, 1\sigma$ ; Fig. 4).



**Figure 3** The  $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$  alteration relationship of feldspar used to derive meteoric water. Meteoric water lines and compiled modern water data are from Passey and Ji (2019). Given are the 1 s.e. bars for the measurements. The black line is the alteration array between unaltered rock and rock in equilibrium with the meteoric water fit to the feldspar data for fractional mixing (Taylor, 1978).



**Figure 4** The  $\delta^{18}\text{O}$ - $\delta\text{D}$  array for feldspar-biotite (this study; Criss and Taylor, 1983) with water/rock (W/R) values of the molar fraction of oxygen given the best fit meteoric water value. W/R values assume fractionation factors of feldspar- $\text{H}_2\text{O} = +2\text{‰}$  for  $\delta^{18}\text{O}$  and biotite- $\text{H}_2\text{O} = -35\text{‰}$  for  $\delta\text{D}$  (Taylor, 1977). Quartz values were not used for calculations.

## Discussion and Conclusions

Most estimates of the isotopic composition of meteoric waters that interacted with crystalline rocks rely on the hydrogen isotope composition of the altered rocks. The isotopic composition of these waters is either calculated directly from  $\delta\text{D}$  values of hydrous minerals and using temperatures from oxygen isotope thermometry (Mulch *et al.*, 2004) or from combined oxygen and hydrogen isotope analyses of rocks and their hydrothermally altered end members and the mixing relationships between them (Criss and Taylor, 1983). Because of the possibility of exchange of hydrogen between minerals and later fluids it is a concern that estimates of the original composition of the meteoric water in these hydrothermal systems is compromised. This difference in calculated meteoric water compositions is measurable and can lead to error in estimates of the isotopic composition of meteoric waters during hydrothermal activity. The error then translates directly to error in palaeoelevation estimates, particularly at low elevations.

For example, we demonstrate that based on the extrapolated mixing relationships in triple oxygen isotope space using feldspar analyses give calculated meteoric water values, assuming  $400\text{ °C}$ , that are  $\sim 2.7$  to  $3.9\text{‰}$  (Table S-2) higher than those determined using combined oxygen and hydrogen isotopes. We note that this difference in calculated meteoric water values is dependent upon the assumed temperature of the hydrothermal system and the choice of the meteoric water lines in  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  space (Table S-1). If we take the maximum temperature of the hydrothermal system of  $400\text{ °C}$  (Criss and Taylor, 1983) will this isotopic difference translate into an elevation difference that is significant? To test this we use the data presented here, with that published on nearby Eocene (38 to 37 Ma) Pioneer core complexes (McFadden *et al.*, 2015) and the Idaho batholith (Criss and Taylor, 1983) (Fig. 1). These three studies all differ in their calculation of the isotopic composition of meteoric waters. Ours is based on triple oxygen and the others rely on hydrogen isotopes. McFadden *et al.* (2015) use the  $\delta\text{D}$  values of micas from detachment faults active in the late Eocene and assumed temperature of formation of these detachments and calculate a  $\delta^{18}\text{O}$  of meteoric water of  $-16.0 \pm 1.5\text{‰}$ . Criss and Taylor (1983) use  $\delta\text{D}$  of biotites and muscovite and the  $\delta^{18}\text{O}$  of feldspar and vein quartz and arrive at the same  $\delta^{18}\text{O}$  of meteoric water of  $-16\text{‰}$ . Using the equations for Eocene lapse rates of Rowley *et al.* (2001), the Eocene elevation of the Idaho batholith was  $4.74\text{ km}$  ( $+0.64/-0.49, 1\sigma$  of the Rowley model) based on hydrogen isotopes. Using the best fit of meteoric water at  $400\text{ °C}$  alteration temperature ( $-11.92\text{‰}$ ) we estimate a lower Eocene elevation of  $3.11\text{ km}$   $+0.31/-0.38$  ( $1\sigma$ ), based on triple oxygen isotopes. At  $1\sigma$  and even at  $2\sigma$  these values do not overlap, though they do overlap at  $2\sigma$  using other meteoric water lines (Table S-2). Nonetheless, we suggest that later hydrogen exchange, at least in this case, results in inaccurate palaeoelevation estimates.

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## Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article2026>.



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