

Modern and ancient hydrosphere-rock interactions constrained from triple oxygen isotope and *in situ* $\delta^{18}\text{O}$ measurements

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We apply triple oxygen isotope ratios to examine water-rock reaction in modern and ancient marine hydrothermal systems. Values of $\Delta^{17}\text{O}$, measured at per meg precision, complement $\delta^{18}\text{O}$ values by enabling study of sources of fluids, mixing, temperature of alteration, progress of water-rock reaction, near-surface boiling and effects of imposed metamorphism. We measured geothermal fluids from the Icelandic systems [see 1] and vent fluids from the Axial Seamount volcano of the Juan de Fuca ridge. These measurements define the trajectories of triple oxygen isotope exchange during water-rock reaction at >250 °C. On average the fluids are 0.01-0.02 ‰ lower in $\Delta^{17}\text{O}$ and 0.5-2 ‰ higher in $\delta^{18}\text{O}$ than the local sources. We also observe ± 20 ‰ fractionation of δD in Icelandic fluids owing to shallow boiling, but no significant $\Delta^{17}\text{O}$ fractionation is observed [1]. The vent fluids from the Axial Seamount system were collected at T from 173 and 341 °C; their Mg concentrations span 2-23 mM and negatively correlate with their $\delta^{18}\text{O}$. The progress of seawater-basalt reaction is defined with the slope of 0.513 ± 0.007 (mean \pm SE, $n=11$) constructed in $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ coordinates and by the lowest $\Delta^{17}\text{O}$ value of -0.026 ± 0.006 ‰. This slope characterizes the contribution of hydrothermal alteration into the triple oxygen isotope budget of terrestrial hydrosphere. In addition to the $\Delta^{17}\text{O}$, we measured $\delta^{18}\text{O}$ *in situ* by SIMS in single quartz crystals that were extracted from the zones of high permeability at the pillow basalt-sheathed dike transition intersected by the IODP drill hole at site 504B. The studied quartz crystals contain CL-bright and CL-dark zones with distinctly different $\delta^{18}\text{O}$ values of 8.0 ± 0.8 ‰ and 15.4 ± 0.5 ‰. They likely record multiple regimes of hydrothermal circulation of seawater at around 330 °C and 160 °C. These *in situ* measurements provide a record of cooling history of the oceanic crust and help to interpret the $\Delta^{17}\text{O}$ data. Ref: [1] Zakharov et al. (2019) Chemical Geology, **530**, 119312