

## The geologic record of $^{17}\text{O}$ and $^{18}\text{O}$ in chert

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The  $\delta^{18}\text{O}$  of authigenic chert is thought to have increased linearly from ~20‰ to ~35‰ over the past 3.5 Ga. This increase can be explained by a progressive shift in the  $\delta^{18}\text{O}$  of seawater through time, a decrease in ocean temperature, which correspondingly, decreases the isotopic equilibrium between chert and water, or the progressive alteration of a primary chert composition by secondary high-temperature fluids. Simply increasing the sample density and making additional  $\delta^{18}\text{O}$  measurements will not resolve this uncertainty. Instead, in addition to the classical isotope measurement, we include data on the  $^{17}\text{O}$  of a suite of Precambrian cherts. This includes samples from 9 Archean, 4 Mesoproterozoic, and 12 Neoproterozoic localities. The mineralogy of each sample is characterized by XRD analysis to provide better geologic context. Additionally, we performed a stratigraphic test by measuring 22 samples from the Tonian Fifteenmile Group in the Yukon. Changes in  $^{17}\text{O}$  are small relative to  $\delta^{18}\text{O}$ , but are statistically significant and provide a new axis of variability that has potential to distinguish a causal mechanism for the long-term isotope evolution in chert. In triple isotope space, we predict variable precipitation temperatures will produce a concave relationship due to the temperature-dependence of the equilibrium fractionation, secondary alteration will produce the inverse relationship, and changing seawater composition would produce a linear relationship that parallels the meteoric water line. In contrast to published records, our data shows a departure from the simple linear increase in  $\delta^{18}\text{O}$  through time punctuated by a Neoproterozoic  $\delta^{18}\text{O}$  depletion that corresponds to relatively heavy  $\Delta^{17}\text{O}$ . This suggests that there is structure in the geologic  $\delta^{18}\text{O}$  chert record that was previously unrecognized - a story further informed by companion  $^{17}\text{O}$  data.