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Large sulfur isotope variation exhibits uncertain biosignature potential at an ancient hydrothermal Mars analog

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Impact crater lakes may have hosted the earliest (>3.5Ga) habitable environments on Earth and Mars. In these locations, impact-induced hydrothermal activity would have provided heat in opposition to a faint young sun and could have sourced compounds thought necessary for prebiotic synthesis as well as bioessential elements needed to sustain life. Interrogating well-preserved segments of Earth's rock record that provide analogs for these settings is thus critical to understanding the earliest life and possible associated biosignatures. For instance, variations >21‰ in stable sulfur isotope ratios ($\delta^{34}S$) throughout Earth's history have been attributed to microbial sulfur cycling, but the uniqueness of this interpretation warrants investigation at sites that are uncommon today but were ubiquitous on early Earth and Mars.

The Miocene Ries crater lake in Germany is one such location, with a backdrop of impact-triggered hydrothermal activity against which the behavior of geochemical proxies offers insights into the relative contributions of biological and physicochemical processes. Suevite—a melt-bearing impact breccia—records a history of hydrothermal alteration in connection with a closed-basin lake, implying that sulfur compounds were subjected to elevated temperatures capable of abiotically fractionating stable isotopes.

Here we present a multi-phase $\delta^{34}S$ study with data from (1)sulfides, bulk sediments, and kerogen extracts of the lake's sedimentary sequence; (2)sulfides from crater-fill breccia; and (3)carbonate-associated sulfates from tufa mounds. The sedimentary sulfides display a maximum $\delta^{34}S$ of 45.1‰, in contrast to the average breccia $\delta^{34}S$ of -15.4‰. The differences in $\delta^{34}S$ between the two host lithologies may have resulted from thermochemical sulfate reduction, microbial sulfate reduction, hydrothermal equilibrium fractionation, or any combination thereof. Scanning electron microscopy reveals that the morphological character of breccia-hosted pyrite is principally angular and fracture-fill in nature, rather than framboidal, thus contributing to ambiguities regarding biological origin. Breccia samples with the highest chromium-reducible sulfide contents (CRS≥1.5 wt%) also have the lowest total organic carbon (TOC≤0.1 wt%), a reverse trend compared to traditional interpretations of microbial sulfate reduction. This study highlights the tenuous biosignature potential in crater lakes of wide-ranging $\delta^{34}S$ values often ascribed to biological cycling in other settings, with implications for astrobiological studies of ancient Earth and Mars.

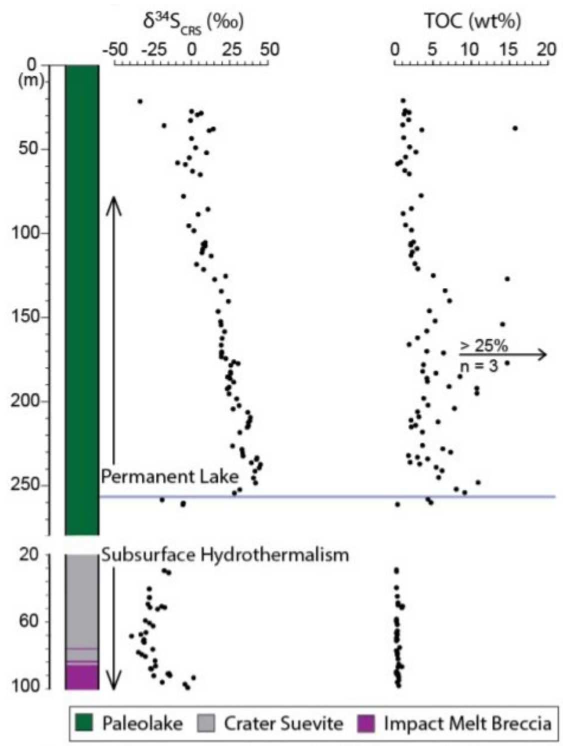

Figure 1: Large variations in $\delta^{34}S_{CRS}$ and TOC (wt%) observed in two stratigraphically related drillcores from the Nördlinger Ries impact crater. Adapted from Tino et al., *in prep*.