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Records of Earth's Past Atmosphere in Ferromanganese Crusts

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Reconstructions of Earth's tropospheric oxygen are important for understanding Earth's atmospheric evolution and the rise of life on this planet. Yet few geological materials preserve records of tropospheric oxygen isotope composition beyond the last ~1 million years of Earth history. Marine hydrogenetic ferromanganese (Fe-Mn) crusts are composed mainly of Mn oxide and Fe oxyhydroxides precipitated from ambient seawater onto hard substrates. Fe-Mn crusts are a useful material for paleoceanography because of their slow and layered formation, which can extend tens of millions of years into Earth's history, and their ubiquitous occurrence throughout Earth's ocean basins. Triple oxygen isotopes have recently gained notice for their ability to discern processes that occur during mineral precipitation. Specifically, new high-precision measurements of $\delta'^{18}O$ and $\delta'^{17}O$ (where δ' denotes a linearized format of δ notation) allow additional insights into mass-dependent fractionation processes, which can be seen in trends of paired $\Delta'^{17}O$-$d'^{18}O$ values (where $\Delta'^{17}O$ values are calculated as deviations from the terrestrial fractionation line). Atmospheric oxygen $D'^{17}O$-$d'^{18}O$ values depend on the relative proportion of photosynthesis to respiration and some contribution from stratospheric intrusions. Fe-Mn crusts have unique $\Delta'^{17}O$ and $d'^{18}O$ values compared to other low-temperature minerals, which is consistent with the incorporation of up to ~50% dissolved O_2 into the Mn portion of the Fe-Mn crust structure (Sutherland et al., 2020; Sharp et al., 2018). This study analyzes the triple oxygen isotope values down the growth axis of a well-studied Fe-Mn crust from the Pacific Ocean to trace tropospheric oxygen isotopic composition over the past 75 million years. We find that the triple oxygen isotope values vary over time. Preliminary data show $\delta'^{18}O$ values range from 5.71 to 13.9 ‰, and $\Delta'^{17}O$ values range from -0.151 to -0.077 ‰ within the Fe-Mn crust. We interpret the triple oxygen isotope variations as reflecting different balances between the processes driving the tropospheric triple oxygen isotope values, providing information on past atmospheric changes over the last 75 million years.