Selenium Biogeochemistry as a Planetary Deep-Time Redox Proxy
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The Earth’s atmosphere and ocean have evolved from an anoxic to an oxic state over the course of the first four billion years of their history. Such global chemical evolution is tightly linked to geological, biological and environmental innovations and catastrophic changes and is therefore a key aspect in unraveling interactions between life and non-life on this and other planets. The timing of the stepwise increases in oxygen concentrations on Earth has been relatively well constrained by the disappearance of mass-independent sulfur isotope fractionation, and the appearance and increase of mass-dependent sulfur isotope fractionation in the geologic record. However, the magnitude of atmospheric oxygenation, as well as the response time of marine oxygenation and of adaptations in biological metabolism is not known.

As a geochemical analogue of sulfur with similar functions in biological metabolism, selenium may also be used as a tracer of redox history. The six stable isotopes of selenium fractionate mass-dependently during biotic and abiotic reduction reactions. But while the dissimilatory reduction of sulfate to sulfide requires strict anoxia, selenate reduction occurs under higher, suboxic Eh conditions. Sulfur and selenium isotope variations combined could thus provide a more precise tool to shed light on local and global oxygenation of Earth’s environment.

Selenium isotopic data can be obtained from Se-poor rock samples using thiol-cotton fiber extraction, continuous-flow hydride generation and multicollector inductively-coupled plasma mass-spectrometry, yielding \( \delta^{76/78}\text{Se} \), \( \delta^{77/78}\text{Se} \) and \( \delta^{82/78}\text{Se} \) values with a 2\( \sigma \) precision \( \leq 0.2\%. \) We collected selenium and sulfur isotope data from a section in Alberta, Canada across the Permian-Triassic mass-extinction boundary, at which time the deep ocean is thought to have undergone a temporary transition from an oxidized to a reduced and euxinic state. The event correlates with a negative excursion in sulfur isotopic composition. A similar trend is observed for selenium isotopes, albeit with a small but significant shift in time, which might be indicative of a gradual shift from an oxic through a suboxic to an anoxic water body. These results emphasize the potential use of selenium isotopes, coupled with sulfur isotopes, to finely constrain the timing and extent of redox events and suggest that such an approach could be fruitful in investigating the early stages of Earth’s and other planets oxidation.