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A shale-hosted selenium isotope record of Paleozoic ocean oxygenation

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Oxygenation of the deep ocean has long been recognized as a necessary condition for the establishment of benthic animal ecosystems. Rich body fossil assemblages in the Ediacaran and Cambrian have thus often been viewed as indicative of dissolved oxygen in bottom waters from this point in Earth history onward. Recent geochemical work, however, has suggested that 1) bottom-water oxygen was intermittent, not permanent, in the Ediacaran and early Cambrian, and 2) protracted atmospheric and marine oxygenation occurred across the Paleozoic, culminating in a fully-oxygenated ocean only after the Devonian establishment of forests (which enabled voluminous organic carbon burial). In light of these findings, it seems low oxygen content in benthic habitats may have limited the expansion of marine animal ecosystems for >100 Myr after the Cambrian Explosion. Recent compilations of vertebrate fossil occurrence might reflect such a redox control, with early jawed vertebrates persisting predominantly in shallow settings until the Devonian. However, existing redox proxy records lack sensitivity at the oxygen thresholds relevant to animals, meaning that we do not yet have direct evidence of a redox control on early animal ecology.

Here we aim to fill that gap with a Paleozoic record of selenium isotope ratios in shales. Selenium (Se) oxyanions are respired at high redox potentials (similar to nitrate and Mn-oxides) with concomitant isotopic fractionation. Modern marine sediments show isotopic evidence of non-quantitative Se oxyanion reduction in bottom waters/porewaters, reflecting a large Se reservoir in a well-oxygenated deep ocean. In contrast, Archean and mid-Proterozoic shales have unfractionated Se isotope signatures reflecting the crustal composition, suggesting quantitative reduction of a small Se oxyanion pool in a dominantly anoxic ocean. In our new record, we find that after intervals of negative δ^{82}Se values in the Ediacaran and early Cambrian, shales return to a predominantly crustal δ^{82}Se composition until the Devonian. This is consistent with a late Cambrian-early Devonian predominance of anoxic deep ocean conditions, which would've enabled quantitative Se oxyanion reduction. Thus, these data are consistent with Devonian deep ocean oxygenation and further indicate that such a redox shift could have sparked the colonization of subtidal habitats by early vertebrates.