Se isotope signature of Paleoarchean and Paleoproterozoic banded iron formations

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The terrestrial and marine evolution and preservation of life are sensitive to changes in redox conditions. Banded Iron Formations (BIF), which have no modern analogues, are chemical sediments deposited from the ancient ocean and may provide clues about the chemical composition and redox conditions of the ocean throughout the Archean. Selenium (Se) is an essential redox-sensitive trace element that may have precipitated into iron oxide/hydroxide phases from Se(IV) species in seawater, and its isotopes are likely to reflect sources and redox processes prior to or during deposition (e.g. microbial and abiotic reduction of Se(VI) to Se(IV)). Here, we show the first investigation of Se content and Se stable isotopic composition ($\delta^{82/76}$Se) from Paleoarchean and Paleoproterozoic BIF formations namely the 3.5 Ga, Iron Ore Group (Tomka-Daitari Greenstone Belt, India) and the 2.4 to 2.2 Ga BIF of the Hotazel and Griquatown Formations (Transvaal Supergroup, South Africa). Overall, the content of Se in BIF is small and varies between 15 to 160 ng g^{-1} in the Hotazel/Griquatown BIFs and 40 to 490 ng g^{-1} in the Iron ore Group. The observed range of δ^{82}Se of Paleoarchean BIF is narrow (δ^{82}Se = -0.75 to 1.09‰). These minor changes in Se isotope composition in the Paleoarchean BIF imply no redox-sensitive Se fluxes and are consistent with a lack of oxidative weathering. On the other hand, the total spread of Se isotope composition in the Paleoproterozoic BIF formation is around 4‰ (δ^{82}Se = -3.4 to 0.52‰). Negative δ^{82}Se values in carbonate-rich Hotazel BIF suggest redox-sensitive Se mobilization during early whiffs of oxygen, possibly coupled to continental weathering of Se. We propose that coupled reduction-adsorption-precipitation processes control the larger variability in Se isotope values in the Paleoproterozoic Hotazel Iron Formation. Further work will determine the variability of Se isotopic composition in the BIF's at the time of the Great Oxidation Event and in sediments across ocean anoxic events. Based on our study, stable Se isotope ratios may help to determine redox conditions in the earliest geological record.