Ferruginous – euxinic – oxic: A three step redox change in the Neoarchean record

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Much of the secular record of sulfur mass independet fractionation (S-MIF) is based on pyrites extracted from a limited number of formations from Western Australia and Southern Africa. Here we present multiproxy evidence for an episodic loss of S-MIF in sulfides from a 2.7 Ga sedimentary record in the São Francisco craton, Brazil. Based on combined proxies, we assigned three phases, in a continous drill core, that track evolving water column redox conditions and changes in ecology. In Phase-I, the stratigraphically older rocks, reactive iron ratios suggest ferruginous conditions. The pyrites have modest S-MIF values ($\Delta^{33}S$ from -0.7 to 2.6‰) and the carbon isotope composition of the iron formations is indicative of carbon fixation by anoxygenic photosynthetic bacteria that oxidized Fe^{2+} ($\delta^{13}C_{org}$ from -27.7 to -17.5‰). Within Phase-II, an intermediate phase characterized by graphite schist, the iron ratios, expansion of the S-MIF ($\Delta^{33}S$ from 2.15 to 3.4‰) and an excess of Mo relative to C_{org} suggest deposition in an anoxic environment with periodic development of euxinic conditions. Phase-III culminates in fully oxic conditions with a loss of S-MIF and emergence of sulfur mass dependent fractionation (S-MDF) with homogeneous $\delta^{34}S$ pyrite values (average = 3.3 ± 0.5‰). The loss of S-MIF in the Archean sulfides of Phase-III was interpreted as a response to increased oxygen levels that lead to an intensification of oxidative weathering. Based on the continous deposition within this drillcore, the development of more oxidizing conditions may have been relatively rapid, reinforcing the model that the transition from S-MIF to S-MDF can happen on rapid geological time scales and was recorded about 400 million years prior to the GOE in the Brazilian craton.