

# **Sedimentary records of MIF-S and redox-sensitive elements indicate the oxygenated early Earth**

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The presence of MIF-S and the low contents of Mo and U in many (not all) Archean-aged sedimentary rocks have been widely considered as “definitive evidence” for an anoxic early Earth. However, the paradigm for MIF-S is questionable because: (a) MIF-S has been found in some recent volcanic ashes, aerosols from coal-burning, and in some post-Archean sedimentary rocks and ore deposits; (b) some products of photochemical- and chemisorption experiments, carried out in O<sub>2</sub>-rich atmospheres, show MIF-S; and (c) the likeliness that, throughout the geologic history, SO<sub>2</sub> from explosive volcanism originated from seawater SO<sub>4</sub><sup>2-</sup> that was produced mostly by the oxidative weathering of pyrite (Ohmoto, 2020). Considering these, here I propose that the MIF-S in Archean and younger materials were produced mostly by: (i) UV photolysis of volcanic SO<sub>2</sub> in an O<sub>2</sub>-rich stratosphere (i.e., above the UV shield) over an O<sub>2</sub>-rich troposphere and (ii) thermochemical SO<sub>4</sub><sup>2-</sup> reduction by organic matter in sediments.

Mo and U contents of ancient shales have been used by previous researchers as accurate measures of *p*O<sub>2</sub> of the contemporaneous atmosphere. However, they have neglected the facts that: (1) more than ~50% of the Proterozoic and Phanerozoic shales, deposited under O<sub>2</sub>-rich atmospheres, have the same Mo and U contents as the Archean shales; (2) nearly all Archean-aged sedimentary rocks have been subjected to high-grade metamorphism, resulting in the losses of >50% of the original contents of organic matter and associated elements (Mo, U etc.); and (3) losses of U by radioactive decay. Here I suggest a new method to estimate the contents of redox-sensitive elements in ancient oceans by examining the concentration ratios of redox-sensitive elements to least mobile lithophile elements, such as Mo/Zr and U/Ti, in sedimentary rocks. My analyses of trace element data on cherts and shales of various geologic ages indicate that the contents of Mo, U and W in the oceans, therefore the atmospheric *p*O<sub>2</sub> levels, have been essentially the same as today since at least ~3.5 Ga ago.