Absence of Mass Independent Sulfur Isotope Fractionation in 2.76 Ga Freshwater and 3.0 Ga Marine Sediments

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The presence of mass independent fractionation (MIF) of S isotopes in pre-~2.3 Ga rocks and the absence of MIF in younger rocks have been regarded by many recent investigators as the best evidence for a dramatic change in the atmospheric oxygen level, from anoxic to oxic, at 2.35 Ga. This is because the MIF of S has been linked to the photochemical reactions of volcanic SO_2 in the absence of an ozone shield to produce S^0 with large positive $\Delta^{33}S$ values (~60 – 70‰) and SO_4^{2-} with negative $\Delta^{33}S$ values (~-23 – -15‰).

We report here the results of mineralogical and geochemical investigations of drill cores from two Archean shale formations, recovered from the Pilbara district, Australia by the Archean Biosphere Project. One core is from the oldest (2.76 Ga) major lacustrine shale (the Hardey Formation) and the other is from a 3.0 Ga marine black shale (the Mosquito Creek Formation). The occurrence, morphology and content of pyrite grains as well as their host rock mineralogy and chemistry suggest that the pyrite crystals in these shales were not detrital grains of igneous rocks, but formed within the host sediments during early diagenetic stage (i.e., diagenetic pyrite) and/or in the overlying water bodies (i.e., syngenetic pyrite). The $\delta^{34}S$ values of ~30 bulk-rock samples vary more than 5‰ in each formation, but their $\Delta^{33}S$ values fall within a range of 0±0.3‰. Therefore, there is **no** evidence of MIF in these formations. The results of our study suggest either: (i) the Archean atmosphere fluctuated between oxic and anoxic, or (ii) large MIF values in geologic samples were not caused by atmospheric photochemical reactions.