3.2 Ga pyrite multi-isotope signatures record a range of redox processes (formation mechanisms) and a heterogenous elemental sulfur source

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The origin and nature of mass independent sulfur isotope variability (MIF-S) in the Paleoarchean rock record continues to be debated. Preservation in pyrite depends on redox processes as well as the values and sign assigned to the products of photolysis. Here we use new pyrite data to empirically assess the validity of conventional and more recent photolysis models [1,2]. The BARB4 core, drilled as part of the ICDP sponsored Barberton Greenstone Belt Drilling project, intersects deep water siliciclastic and orthochemical sediments of the 3.26-3.23 Ga Lower Mapepe Formation, Fig Tree Group. Pyrite is common in disseminated, layered, agglomerate and late-stage vein forms in mudstones intercalated with BIFs. Here we use combined SIMS multiple S (δ^{34}S, Δ^{33}S, Δ^{36}S) and Fe (δ^{56}Fe) isotope data to identify the origin of the pyrite and constrain the δ^{34}S/Δ^{33}S photolysis array from which the sulfide was sourced. Δ^{33}S fluctuates from 0.42 to 2‰, but is constant at each stratigraphic depth. All samples lie on the Archaean reference Δ^{33}S/Δ^{36}S array. δ^{34}S shows limited but reproducible mass-dependent fractionation of up to 4‰. The lack of correlations between Δ^{33}S and δ^{34}S suggests the absence of post-depositional mixing of different sulfur sources. Intra-grain δ^{56}Fe variability is up to 2‰ within individual pyrite populations. We interpret the disseminated pyrite to have precipitated from porewater resembling Archaean seawater δ^{56}Fe (~0‰), whereas layered and agglomerate pyrite (average δ^{56}Fe= +1‰) originated from the sulfidization of Fe oxides. Our data show that inversion of the atmospheric MIF-S signature in oxidized and reduced photolysis products, as suggested by [2] was unlikely and support a conventional model in which Δ^{33}S heterogeneity in the sulfide was derived from photolytic elemental S.

[1] Farquhar *et al*. (2000), Science **289**, 756-758 [2] Claire *et al*. (2014), GCA, **141**, 365-380