Fe and S isotope constraints on redox conditions associated with barite deposits from the 3.2 Ga Mapepe Formation (South Africa)

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The presence of extensive barite sedimentary deposits in the Archean record is intriguing since this type of sediment requires high availability of dissolved sulfate (SO_4^{2-}), the oxidized form of sulfur, although most authors suggest that this period was dominated by reducing conditions. In order to assess the redox state of the paleo-atmosphere and -oceans, we examined Fe and S multiple-isotope compositions in a sedimentary sequence from the 3.2 Ga-old Mendon and Mapepe Formations (Kaapvaal craton, South Africa), recovered during the Barberton Barite Drilling Project (BBDP2). Major and trace elements were also analyzed to evaluate potential diagenetic and/or metasomatic modifications. Bulk rock δ^{56}Fe values show a large range from -2.04 ‰ in Fe sulfide-dominated barite beds, to 2.14 ‰ in Fe oxides-bearing cherts. δ^{34}S values of bulk sulfides vary between -10.84 and 3.56‰, with Δ^{33}S generally in a limited range from -0.35 to 0.40‰ (except two black cherts from Mendon at 1.69 and 2.55 ‰).

Iron isotope variations, together with major and trace element correlations, illustrate that samples from Mendon experienced metasomatic Fe-carbonate precipitation. In contrast, samples from Mapepe were strongly silicified and tend to preserve primary geochemical and isotope fingerprints. Highly positive δ^{56}Fe values recorded in primary Fe-oxides support very partial Fe oxidation in a reducing oceanic environment ($O_2 < 10^{-3}$ μM), but are incompatible with a model of complete oxidation at the redox boundary of a stratified water column. Iron oxide precipitation at such low oxygen level was likely mediated by anoxygenic photosynthesis, and/or abiotic photo-oxidation process. The mass-independent sulfur isotope signal recorded in sulfides can be attributed to SO_2 photochemical dissociation, thus supporting an O_2-deprived atmosphere (< 10^{-5} PAL). Overall, Fe and S isotope compositions thus record global anoxic conditions in the 3.2 Ga-old sediments associated with barium sulfate deposits.