

Multiple sulfur isotope analyses of sulfides from Paleoproterozoic (2500 to 1800 Ma) sediments by ion microprobe

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Geochemical evidence reported from Paleoproterozoic sediments has been used to evaluate the transition from the anoxic Archean atmosphere to an oxygenated atmosphere. Multiple sulfur isotopes (^{32}S , ^{33}S , ^{34}S) in sedimentary sulfides and sulfates are an especially sensitive proxy to monitor this transition (Farquhar et al., 2000), such that the appearance and duration of the Paleoproterozoic “Great Oxidation Event” (Holland, 1994) can be investigated using mass independently fractionated (MIF) sulfur isotope systematics expressed as $\delta^{33}\text{S}$. Here we report data from 84 individual analyses of pyrite, pyrrhotite and chalcopyrite on a new suite of 30 different samples from Finland, South Africa, Wyoming and Ontario (Canada). The samples, spanning ~ 600 Ma, were measured using a high-resolution secondary ion microprobe in multicollection mode (Mojzsis et al., 2003). Our results demonstrate that MIF sulfur isotopes ceases between 2.52 and ~ 2.3 Ga, independently confirming previous observations (e.g. Bekker et al., 2004). Oxygen levels in the atmosphere increased above $\sim 10^{-5}$ PAL (present atmospheric level; Pavlov and Kasting, 2002) during this ~ 200 Ma interval, and before the onset of the Paleoproterozoic $\delta^{13}\text{C}_{\text{carb}}$ excursion(s) (Karhu, 1993). Our results also point to the presence of microbial sulfate reduction at that time and possible fluctuations in the concentration of dissolved seawater sulfate. These fluctuations were possibly due to interplay between a number of important oxygen sinks in the Paleoproterozoic such as

high concentrations of reduced cation species in the upper ocean (e.g. Fe^{2+} , Mn^{2+}), crustal sulfides, organic matter and reduced atmospheric gases (e.g. methane).