

Quadruple sulfur isotope analysis of ~3.0 Ga Pongola Supergroup

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Multiple sulfur isotope ratios of various ages of minerals have constrained composition of Earth's early atmosphere. Sulfur mass-independent-fractionation (MIF) is observed only in geological records older than ~2.0 Ga, but not in younger strata (e.g., Farquhar and Wing, 2003). This unique MIF signature is known to be caused by photochemical reactions of sulfurous gas, and thus suggests oxygen-poor atmosphere (i.e., weak UV shielding) before 2 Ga. However, recent investigations demonstrated that no large MIF has been observed in a period from 3.0 to 2.8 Ga (Ohmoto et al., 2006; Ono et al., 2006a). This implies a possibility that the oxygen content of the atmosphere may have increased tentatively at around 2.9 Ga (Ohmoto et al., 2006; Ono et al., 2006a). Alternatively, Farquhar et al. (2007) interpreted that presence of 'weak' MIF at 2.9 Ga do not imply oxygen rise, but change of atmospheric chemistry. In order to evaluate these scenarios, it is essential to extend multiple sulfur isotope data for geologically and petrographically well-characterized 3.0 to 2.8 Ga sedimentary rocks. Here, we report quadruple sulfur isotope analysis of wide range of lithotypes (conglomerate, sandstone, siltstone, dolomitic sandstone, arenaceous dolostone and stromatolitic dolostone) occurring in 2985-2837 Ma Nsuzi and Mozaan Groups, South Africa. High precision analysis of both D33S and D36S is helpful to distinguish MIF from MDF (Mass-Dependent-Fractionation). The D33S values of sulfides of Mozaan Group are from -0.41 to 0.13 permil, which are similar to those reported by previous studies. Those of Nsuzi Group are from -0.11 to 0.35 permil, which are similar to those of the upper Mozaan Group. This means that the feature of small D33S signatures within 0.5 permil was more global and lasting longer than previously thought. As a result of examining D33S/D36S relationships, it was found that 5 samples of Mozaan Group and 7 of Nsuzi Group show small but clear MIF signature. Furthermore, isotope ratios of Nsuzi and Mozaan sulfides exhibit two mutually distinctive areas in a plot of D33S vs D36S irrespective to their lithological variety, suggesting temporal (not geographical) change of chemistry responsible for these MIF. Our results do not conflict with 'the oxygen poor atmosphere (pO₂ below 10⁻⁵PAL) model', in which MIF signatures was produced by photochemistry in the oxygen poor atmosphere and preserved in sediments without re-mixing. It is plausible that the sulfate concentration of 3.0-2.8 Ga seawater was low enough to remain MIF signatures. However, the D33S and D36S values of sulfides in carbonate of Nsuzi Group are very similar to those of modern sulfate aerosols (Romeo&Thiemens, 2003). This implies the mechanism to produce the MIF of Nsuzi sulfide is similar to that of present day aerosol formation. Hence, Nsuzi stage may represent a period of low but relatively rising atmospheric oxygen (pO₂ above 10⁻⁵PAL).