## The Great Oxidation Event preceded a Paleoproterozoic 'snowball Earth'

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The temporal relationship between the Great Oxidation Event (GOE) and a Paleoproterozoic 'snowball Earth' glaciation remains unresolved. We present new, temporally constrained, quadruple sulfur isotope measurements ( $\delta^{34}$ S,  $\Delta^{33}$ S and  $\Delta^{36}$ S) from the Paleoproterozoic Seidorechka and Polisarka Sedimentary Formations in NW Russia. The older Seidorechka Sedimentary Formation preserves negative  $\Delta^{33}$ S values and a  $\Delta^{36}$ S/ $\Delta^{33}$ S slope of  $-1.86 \pm 0.47$ , consistent with Archean values. The vounger Polisarka Sedimentary Formation preserves mass-dependent signals, with a  $\Delta^{36}S/\Delta^{33}S$ slope of -8.8 and negative  $\delta^{34}$ S values. The transition from mass-independent (S-MIF) to mass-dependent fractionation of S isotopes (S-MDF) is bracketed by established radiometric ages of  $2501.5 \pm 1.7$  Ma and 2434 ± 6.6 Ma. Thus, the S-MIF/S-MDF transition predates both the Polisarka glacial deposits and the ~2424 Ma Makganyene 'snowball Earth' diamictite in South Africa, supporting the hypothesis that atmospheric oxygenation caused the collapse of a methane-dominated greenhouse and triggered global glaciation.