## Low atmospheric pO<sub>2</sub> in the aftermath of the oldest Paleoproterozoic glaciation

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The rise of the atmospheric  $pO_2$  and the occurrence of Paleoproterozoic glaciations may be related via oxidation of atmospheric methane and subsequent collapse of greenhouse conditions (Pavlov et al., 2000). A lack of a significant non mass-dependent signal in S isotopes of sulfides from the shales both underlying and overlying the first glacial diamictite of the Huronian Supergroup (Wing et al., 2004) supports this interpretation and provides a constraint on the minimum atmospheric  $pO_2$ . However, constraints for the maximum atmospheric  $pO_2$  and variations in atmospheric  $pO_2$  during the Paleoproterozoic glacial epoch are lacking.

Here we report S isotope values of pyrite grains in conglomerates of the siliciclastic Mississagi Formation of the 2.45-2.22 Ga Huronian Supergroup that were deposited between the first and second glaciations. Pyrite grains have a range from -7.2 to +6.0 ‰ in  $\delta^{34}$ S and from -0.4 to +1.2 ‰ in  $\Delta^{33}$ S on the scale of hand samples. Mississagi conglomerates with pyrite grains occur in the entire Huronian Basin, indicating regional distribution of pyriferous facies in mature sediments.

The sulfur isotope data are consistent with the detrital origin of the pyrites from conglomerates with their source in Archean greenstone belts and imply low atmospheric  $pO_2$  limiting oxidative pyrite dissolution. In contrast, S and Fe isotope values of pyrites in black shales deposited after the second Paleoproterozoic glaciation in South Africa indicate oxidative sulfide weathering and a redox-stratified ocean (Bekker et al., 2004; Rouxel et al., 2005). The emerging picture is that a stepwise increase in the atmospheric  $pO_2$  throughout the Paleoproterozoic glacial epoch was accompanied by a decrease in the atmospheric  $pCH_4$  and an increase in the atmospheric  $pCO_2$ .

## Before the rise of oxygen: Multiple sulfur isotope systematics in the late Archean basins in South Africa and Australia

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The late Archean is the time when the Earth's early biosphere set the stage for the subsequent oxygenation of the Earth's atmosphere. Late Archean atmospheric and oceanic chemistry are critical in understanding the series of events that took place in this key period of the Earth's history.

We will report our results of multiple sulfur isotope investigation in the two late Archean basins, the Griqualand Basin, South Africa, and the Hamersley Basin, Western Australia. Intra- and inter-continental stratigraphic correlations and basin reconstruction allow us to document temporal and geographical variation of the multiple sulfur isotope ratios.

We will discuss sub-mm to formation scale multiple sulfur isotope variations determined by a newly developed laser fluorination continuous-flow IRMS.

These measurements record a combination of both biological (mass-dependent) and atmospheric (massindependent) isotope fractionations. We will discuss how such multiple sulfur isotope variations correlate with the depositional environment and the sedimentological evolution of the two basins.

Our reconstruction of Archean sulfur cycle places redox gradients in the late Archean oceans. We will discuss implication of the redox gradient and its relation to the subsequent oxidation event of the Earth's atmosphere.