NEW QUADRUPLE SULPHUR ISOTOPE RECORDS FROM THE DUITSCHLAND/ROOIHOOGTE FORMATION(S): (RE)DEFINING THE STRUCTURE OF THE GREAT OXIDATION EVENT.

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The early Palaeoproterozoic oxygenation of Earth's surficial environment fundamentally altered the chemistry and ecological structure of our planet—Rendering Earth an, as yet, unique planet, whilst "lighting" the fuse for the emergence of micro- and macroscopic life. Based on numerous geological and geochemical arguments, it is widely believed that Archaean atmospheric O_2 was low (< 10^{-5} present atmospheric level; PAL), rising irreversibly to a fraction of present-day levels during the Great Oxidation Event [1]. Recently, however, this canonical view of planetary oxygenation has been questioned by analyses of ~3.0–2.5 billion-year-old (Ga) sediments, which have been interpreted to reflect transient or localized oxygenation [e.g., 2, 3] as well as periods of more reduced atmospheric composition directly prior to the GOE [4, 5]. Assimilated these studies hint at a complex atmospheric evolution that we are only beginning to comprehend.

Despite the hypothetically multifaceted atmospheric evolution, the emerging picture is obstructed because most geochemical proxies record oceanic conditions that are only indirectly tied to the atmosphere via differing, and often unknown, sensitivities. Fortunately, the sedimentary S-isotope record is implicitly linked to the redox state of the atmosphere in multiple ways [e.g., 6]:

1. Shortwave UV photolysis (λ = 180–220 nm) of SO_2 has been shown to produce S-MIF requiring the absence of an atmospheric O_2/O_3 photon filter.
2. Atmospheric export of S-MIF, and its ultimate preservation, requires atmospheric sulfur deposition via at least two exit channels, which are homogenized at O_2 concentrations exceeding 10^{-5} PAL, eliminating the S-MIF signal.
3. Oceanic mixing, against a moderate sulfate reservoir, would dilute and eradicate the S-MIF signature.

Consequently, the observed bi-modal operation of sulphur isotope fractionation entombed in the geological record—shifting from mass independent fractionation (MIF; $\Delta^{33}S$ and $\Delta^{36}S \neq 0$) to mass dependent fractionation (MDF; $\Delta^{33}S$ and $\Delta^{36}S = 0$) [7]—is taken as the most robust evidence for the rise O_2 above 10^{-5} PAL and the straigraphic marker of the GOE.

Despite the potential diagnosticity of S-isotope fractionation, our temporal understanding of the GOE has been hindered by the lack of outcrop of the appropriate age and a lose chronostratigraphy. Recent work, exploiting three cores from the Transvaal Supergroup (South Africa), however, has helped to close this knowledge gap and now places the GOE stratigraphically in the Upper Duitschland Formation. Furthermore, these records imply the shift in atmospheric composition was rapid (1–10 Myr), unidirectional and an oxygenated atmosphere was established by 2.33 Ga [8].

In this contribution we seek to test these hypotheses, and refine the findings of Luo et al. [8], reporting emerging quadruple S-isotope datasets from four stratigraphically equivalent, recently drilled, cores from the Transvaal Supergroup (AGP-1, AGP-2, ANW-1 and ADL-1). We anticipate that these cores will contain continuous GOE expressions, and will yield the highest resolution quadruple S-isotope records over this critical juncture in Earth History. Forming the backbone of the ongoing chemostratigraphy, these cores will reveal the rate and structure of planetary oxygenation allowing us to refine and test emerging hypothesis concerning the causes and consequences of planetary oxygenation. Ultimately a thorough and complete understanding of Earth's oxygenation will help guide our search for life in the broader universe.

References: [1] Lyons et al. (2014) *Nature,* 506, 307-315. [2] Anbar A. D. et al. (2007) *Science,* 317, 1903–1906. [3] Kendall et al. (2015) *Sci. Adv.,* 1, DOI: 10.1126/sciadv.1500777. [4] Zerkle A. L. et al. (2012) *Nature Geosci.,* 5, 359–363 (2012) [5] Izon G. et al. (2016) *EPSL*., 431, 264–273. [6] Farquhar J. et al. (2011) *Photosynth. Res.,* 107, 11–36. [7] Farquhar J. et al. (2000) *Science,* 289, 756–758. [8] Luo G. et al. (2016) *Sci. Adv.,* 2, DOI: 10.1126/sciadv.1600134.