Mass-independent sulfur isotope effects: Implications for the rise of the atmospheric oxygen

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Several lines of geological and geochemical evidence point to a change in the oxidation state of the atmosphere between 2.45 and 2.22 Ga. Syngenetic pyrite in highly carbonaceous shales of the 2322 ± 15 Ma Rooihoogte and Timeball Hill formations, South Africa, have $\Delta^{33}S_{ln}$ values less than 0.33‰ and a wide range of highly negative $\delta^{34}S$ values. These observations are consistent with the notion that atmospheric pO_2 was larger than 10^{-5} PAL during the growth of this pyrite. The presence of mass independent fractionation (MIF) signals >1‰ in sulfur isotopes of sulfides from 2470 Ma sediments indicates that O_2 levels began to rise between 2470 and 2322 Ma. Rounded pebbles of sideritic iron-formation at the base of the Rooihoogte Formation and an extensive and thick ironstone consisting of hematitic pisolites and oolites in the upper Timeball Hill formation indicate that atmospheric O_2 rose significantly - perhaps for the first time - during the deposition of the Rooihoogte and Timeball Hill formations that are sandwiched between what are probably the second and the third of the three Paleoproterozoic glacial events.

Bekker, A., Holland, H. D., *Wang, P.-L.*, Rumble, D. III, Stein, H. J., Hannah, J. L., Coetzee, L. L. and Beukes, N.J. (2004) Dating the rise of the atmospheric oxygen: Nature, 427, 118-120.