

## **Cu isotope evidence for aerobic methanotrophy in the Late Archaean**

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The Great Oxidation Event (GOE, c.2.45 Ga) marks a fundamental change in the interaction between the biosphere, atmosphere, and Earth's surface environment. Recent studies suggest that Earth's anoxic pre-GOE atmosphere was also heavily influenced by biological feedbacks. Notably, recent geochemical records suggest that a hydrocarbon-rich haze periodically formed as a result of enhanced methane fluxes from the biosphere, triggered by increased carbon export to sediments [1, 2].

Copper isotopes provide a potential proxy for biological methane cycling, as copper is a bioessential trace metal and a key element in the aerobic oxidation of methane to carbon dioxide (methanotrophy). In addition, copper isotopes are fractionated during biological uptake [3]. Here, we explore the potential of copper isotopes as a proxy for aerobic methanotrophy in the rock record.

We present a high-resolution copper isotope record measured in a suite of shales and carbonates from core GKF01, through the ~2.6 – 2.5 Ga Campbellrand-Malmani carbonate platform. Our data show a 0.8‰ range in copper isotope composition and a negative excursion that predates the onset of the haze event. Examined alongside previously published carbon and sulphur isotope records, these data demonstrate a clear role for aerobic methanotrophy in the incorporation of methane into Late Archaean sediments.

[1] Zerkle et al., 2012, *Nature Geo*; [2] Izon et al., 2017, *PNAS*; [3] Navarrete et al., 2011, *GCA*.