Did oceanic biogenic methane cycling regulate the evolution of Early Earth atmospheric chemistry? C. Thomazo, UMR-CNRS 6282 Biogéosciences, Université de Bourgogne, Dijon, France (correspondence: christophe.thomazo@u-bourgogne.fr).

One of the most remarkable changes in the Earth surface chemistry of our planet history was the biologically induced pervasive oxygenation of the ocean and atmosphere between around 2.45 to 2.32 Ga. This event, namely the Great Oxidation Event (GOE, [1]), is underlined in the sedimentary record by the disappearance of mass independent fractionation of sulfur isotopes which is a robust geochemical signature of a low oxygen level ($<10^{-5}$ times the present atmospheric level; [2]) in Earth's atmosphere and surface environments.

In the last decade, a growing number of studies using geochemical proxies capable of tracing atmosphere and ocean paleo-redox conditions suggests localized and transient oxygenation of the marine environment as early as 300 Ma before the GOE [3-4]. The idea of a pre-GOE "whiff" of oxygen in terrestrial environment is in line with molecular biomarkers evidence for an early rise of oxygenic photosynthetic bacteria at around 2.7 Ga [5]. However, strong uncertainties remain regarding the extend of di-oxygen production and its consequences onto the oceanic and atmospheric redox balance at that time.

In order to explore atmospheric and oceanic chemistry before the transition toward an oxidizing Earth, we report the results of a detailed carbon (^{12}C, ^{13}C), sulfur (^{34}S, ^{33}S, ^{36}S) and nitrogen (^{14}N, ^{15}N) isotopic study of well preserved Neaorchean (2.7 to 2.6 Ga) sediments from the Pilbara craton (Australia), the Belingwe Greenstone Belt (Zimbabwe) and the Superior carton (Canada).

We suggest that a protracted oceanic oxygenation starting at around 2.7 Ga might have widely impacted marine biogeochemical cycles and triggered the evolution of methane oxidizing bacteria (methanotrophs) but that Neoarchean atmospheric chemistry remained weakly reducing at that time. In particular, paired carbon isotopes of carbonate and organic matter coupled with mass independent fractionation of sulfur isotopes record suggest that biogenic methane fluxes between ocean and atmosphere might have strongly influenced the magnitude and signs of mass independent fractionation of sulfur isotopes and the overall atmospheric sulfur chemistry on the Early Earth. We propose that geochemical signatures of biologically induced changes in atmospheric chemistry could thus be recorded before oxygen rise using multiple isotopic studies including for instance carbon, sulfur and nitrogen.

[1] Holland H. D. (2006) *Philos. Trans. R. Soc., B 361*, 904–916. [2] Pavlov A.and Kasting J. (2002) *Astrobiology 2*, 27–41. [3] Anbar A.D. et al. (2007) *Science 317*, 1903–1906. [4] Thomazo C. et al. (2011) *Geobiology 9*, 107–120. [5] Sessions et al. (2009) *Curr. Biol. 19*, 567-574.