

Carbon isotope tracing of autotrophic metabolisms immediately after the Paleoproterozoic great oxidation event. Genming Luo¹, Shuhei Ono¹, Nicola Ferralis², Nicolas J. Beukes³, and Roger E. Summons¹, 1. Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue E25-608, Cambridge, MA 02139, USA, 2. Department of Material Sciences and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA, 3. Paleoproterozoic Mineralization Research Group, Department of Geology, University of Johannesburg, P.O. Box 524, Auckland Park 2006, South Africa. Correspondance should be addressed to Genming Luo, E-mail: gmluo@mit.edu

Due to large but variable carbon isotopic fractionation during different autotrophic processes, the carbon isotope compositions of organic matter ($\delta^{13}\text{C}_{\text{org}}$) can be used to evaluate carbon cycles in deep time [1]. A significant perturbation of the carbon cycle has been proposed to have occurred after the Paleoproterozoic great oxidation event (GOE) on the basis of inorganic C-isotope ($\delta^{13}\text{C}_{\text{carb}}$) records in the Duitschland Formation in South Africa [2-3]. However concomitant $\delta^{13}\text{C}_{\text{org}}$ data do not show significant variation [2]. Here we report a high-resolution $\delta^{13}\text{C}_{\text{org}}$ record of the upper Rooihogte Formation recovered from the core KEA-4 drilled near Carletonville, South Africa. The Rooihogte Formation is widely thought to be correlative with the Duitschland Formation in the Duitschland area. We studied the upper Rooihogte Formation that are correlated with the upper Duitschland Formation based on the lithostratigraphic similarities and distinctive sequence boundary in both areas [2].

The $\delta^{13}\text{C}_{\text{org}}$ values of the upper Rooihogte Formation are in the range from -31.7‰ to -35.4‰, with a slight negative shift, from \sim -32‰ to $<$ -35‰, in the uppermost Rooihogte Formation. These $\delta^{13}\text{C}_{\text{org}}$ values are significantly lower than those observed previously for the upper Duitschland Formation, which vary around -23‰ [2]. Early studies suggested that such a difference might be the result of the higher thermal maturity of the Duitschland Formation since preferential loss of ^{12}C and isotope exchange between co-existing carbonate and organic matter during thermal metamorphism [4]. It has been shown, however, that an increase of about 3‰ $\delta^{13}\text{C}_{\text{org}}$ can follow from a decrease in H/C ratio from 0.8 to 0.1 [5]. Thus a $>$ 10‰ difference is hard to be ascribed simply to different thermal regimes in these two areas.

Here we propose that different $\delta^{13}\text{C}_{\text{org}}$ values in two sections represent different microbial communities across the Kaapval Craton. Paired $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ suggest that the carbon isotope fractionation ($\Delta^{13}\text{C}$) was \sim 30‰ in the upper Duitschland Formation, whereas the $\Delta^{13}\text{C}$ in the Rooihogte Formation is $>$ 40‰ if we assume that the $\delta^{13}\text{C}_{\text{carb}}$ was nearly the same as that of the Duitschland area, as modeled by Hotinski et al. [6]. The lower $\Delta^{13}\text{C}$ value suggest that

organic carbon sedimented in the Duitschland area largely derived from photoautotrophic microbes such as cyanobacteria. The larger fractionations observed in the upper Rooihogte Formation suggest that it contains a higher proportion of organic matter from anaerobic microbes, such as methanotrophs and phototrophic Fe^{2+} -oxidizers [1, 7] while the wide range of $\delta^{13}\text{C}_{\text{org}}$ in the upper Duitschland Formation could reflect variations in microbial composition. Our data further suggests that the ocean was stratified directly after the GOE and that organic matter from Duitschland area was derived from shallow water communities whereas samples from core KEA-4 area are representative of distal deeper water environments [8]. Moreover, the sediments encountered in the KEA-4 represents a deepening upward sequence where compositional changes in organic matter are reflected in subtle changes in Raman spectra and in the distributions of pyrolysis products.

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