

# Carbon isotopic ratios in early Proterozoic: C fixation pathways and the fluctuation of redox boundary

# Naohiko Ohkouchi[1]; Kazuhisa Goto[2]; Takemaru Hirai[3]; Shogo Tachibana[4]; Shinji Yamamoto[5]; Joseph L. Kirschvink[6]; Yukio Isozaki[7]; Nanako, O. Ogawa[1]; Ryuji Tada[8]; Eiichi Tajika[9]

[1] IFREE; [2] Earth and Planetary Sci., Univ. Tokyo; [3] Earth and Planetary Sci., Tokyo Univ.; [4] Earth and Planet. Sci., Univ. of Tokyo; [5] Earth and Planetary Sci., Tokyo Univ; [6] GPS, Caltech; [7] Earth Sci. & Astron., Univ. Tokyo Komaba; [8] DEPS, Univ. Tokyo; [9] Dept. Earth Planet. Sci., Univ. of Tokyo

In this study we report carbon isotopic compositions of sedimentary carbonate and organic matter in Huronian and Snowy Pass Supergroups deposited in early Proterozoic (2.4-2.2 Ga) collected from SE Canada and Wyoming, respectively. So far we have measured 85 samples for organic matter and 32 samples for carbonate. To our knowledge this is the first study reporting the isotopic compositions of both carbonate and organic matter from these supergroups. Although carbon isotopic compositions of organic matter mostly ranged from -24 to -22 per mil, those from the uppermost sections of both supergroups are enriched in  $^{13}\text{C}$  by 5 to 10 per mil relative to those from other sections. In these sections, isotopic compositions of some samples are as heavy as -5 per mil. By contrast, mean isotopic composition of carbonate carbon is as heavy as +24.1 per mil ( $n=12$ ) in the upper part of the Huronian Supergroup (Nash Fork Fm.), confirming the previous report. These samples completely cover three glaciation periods in the early Proterozoic. The observed isotopic excursion in organic matter can be correlated with the timing after the third glaciation, which has been hypothesized as a Snowball Earth.

The heavy isotopic compositions in carbonate carbon have to be carefully checked whether the original isotopic signatures were recorded or not. However, if assuming that they record more or less original isotopic signature, the apparent isotopic fractionation during the photosynthesis could have ranged from -50 to -9 per mil, which is substantially wide variation relative to those of organic matter produced in most modern environment (-30 to -20 per mil). For samples whose apparent isotopic fractionation is larger than -30 per mil, methanotrophs may have contributed significantly. An alternative explanation which can explain both large and small isotopic fractionation is that the organic matter was not fixed through Calvin cycle but different pathways. They may have been derived from either reductive acetyl-CoA pathway whose isotopic fractionation is as large as -50 per mil relative to the inorganic carbon or reverse TCA cycle and 3-hydroxypropionate pathway whose isotopic fractionations are around -10 per mil. In modern environment, these pathways for carbon fixation are observed in organisms like anammox, green sulfur bacteria, and green non-sulfur bacteria, respectively, which live only in strictly anaerobic environment. These considerations lead us to a speculation that a  $\text{O}_2/\text{H}_2\text{S}$  interface often existed in the euphotic zone in the early Proterozoic.

