Constraints on primary producers at 3.2 Ga Barberton oceans: geological and geochemical studies on chert samples from the Sheba Hills area, Barberton

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The organic matter (OM) in Archean sedimentary rocks records biological activities in concern with the ocean environment at that time. A bunch of previous studies treated with the banded Iron Formations (BIFs) to know the Archaean biosphere, however, the occurrences of OM itself have been ignored. This is because the OM in the BIFs are easy to be decomposed and hardly left in the iron-rich layers. To approach this problem, black chert and BIFs in the ca. 3.3 to 3.2 Ga upper Onverwacht Group and Fig Tree Group which have been suffered a low-Green schist metamorphism, were investigated in the present study to constrain the primary producers at that time in the relation to occurrences of OM.

Black chert layer was conformably overlaid by the BIF layer, indicating that they were precipitated in the same sedimentary basin. Most black chert samples preserved sedimentation layers made by OM in millimeter of scale. Fine grains of organic matter are also found in the matrix of chert. A part of black chert was brecciated and contains quartz veins, which host aggregates of organic matter. Vein structures of OM were also found in black chert, suggesting that the post depositional migration of OM during early stage of diagenesis. Fine particles of OM, in approximately 1-micron meter in diameter, were commonly observed in the microcrystalline quartz among iron minerals in the iron layers of BIFs. Those OM were syndepositional with BIFs, and most likely represent the OM of primary producers. Such occurrence of OM in BIFs have never been reported in previous studies.

Concentrations of total organic carbon (TOC) in the examined samples were ranged from 0.3 to 0.4 wt% for black chert, and 0.0 to 0.2 wt% for BIF samples. Detectable amount of OM was left in BIF samples, were consistent with the observations above.

Morphological observations of kerogen samples, isolated from both black chert and BIF samples, were performed by using FE-SEM, revealing that kerogen exhibited similar fluffy forms regardless of the rock types. The Raman spectrum analysis on kerogen samples indicated that they have the same metamorphic temperature as 350 ˚C, which was consistent with the metamorphic grade in the studied area (lower green schist).

Carbon isotope compositions ($\delta^{13}C$) values of black chert were ranged from -27.7 to -20.7 ‰(VPDB), and those of BIF samples were -30.2 to -25.9 ‰(VPDB). Black chert and most BIFs have relatively homogeneous isotope compositions, regardless of difference in sampling localities and lithologies. In particular, there was no distinct difference in $\delta^{13}C$ values between iron layer and chert layer in BIF samples implying that anoxygenic photosynthesis (e.g., anaerobic phototrophic iron oxidizing bacteria) could not be the primary producer in the 3.2 Ga Barberton ocean. These $\delta^{13}C$ values most likely represent the Calvin-Benson type carbon fixation was more major in 3.2 Ga oceans, meaning that oxygenic photosynthetic bacteria, e.g., cyanobacteria, was the primary producer. On the other hand, A part of BIF samples showed the ^{12}C-enriched value (such as -30.2 ‰). This may correspond to the fluctuation of carbon isotopic compositions of the carbon reservoirs in the contemporary ocean. Such

specific reservoirs were most likely formed by recycling of carbon derived by degradation or oxidation of sedimentary OM in oxic/anoxic stratified oceans.

Keywords: Archean, Barberton Greenstone Belt, Banded Iron Formation (BIF), Black chert, Organic matter

