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## Geochemical signatures pointing to an oxygenated shallow ocean 3.2 billion years ago

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Timing of the emergence of oxygenic photoautotrophs (e.g., cyanobacteria) is critical to understanding the evolution of life and the earth's surface environments. Yet, no palaeontological or biochemical signature in rocks has provided unequivocal evidence for the emergence of cyanobacteria in the Archean era. Recently, Javaux et al. (2010) discovered large, well-preserved microfossils, which are possibly the remnants of eukaryotes, from sedimentary rocks of the Moodies Group, South Africa (-3.2 Gyr). Since the emergence of eukaryotes likely requires molecular oxygen, cyanobacteria is expected to have been evolved before 3.2 Gyr if the microfossils are indeed the remnants of eukaryotes. Therefore, the objective of this study was to find geochemical signatures for the emergence of cyanobacteria in a shallow ocean environment from the same stratigraphic unit as that Javaux et al. found the microfossils.

We collected 26 sample of the Moodies Group both from outcrops and underground mining sites (e.g., Sheba gold mine) in the Barberton Greenstone Belt, South Africa. Sedimentary rock samples from the Sheba mine were divided into Magnetite-Rich Shale (MRS) group and Banded Chert (BC) group. Samples in the MRS group contain quartz, magnetite, hematite, chlorite, biotite, and chromite. While fine-grained hematite (less than 5 micro meter in diameter) is interpreted as a primary mineral in the rock, large-grained (more than 100 micro meter in diameter) magnetite is interpreted as a secondary mineral transformed from hematite during diagenesis. All chromites observed in the MRS group is euhedral and overgrown by magnetite. The boundary between chromite and magnetite is sharp. These characteristics of the chromites in the MRS group indicate that they were syn-genetically formed during diagenesis. On the other hand, samples in the BC group contain quartz, siderite, chlorite, biotite, and chromite. Chromites in the BC group are included in silicate minerals (e.g., chlorite and biotite), and often unehedral crystals.

Chemical compositions of the bulk samples in the MRS group showed that U/Th ratios have a negative correlation with both Cr/Ti and  $Fe_{tot}/Ti$  ratios. This correlation is very difficult to explain if minerals containing these elements were detrital in origin, because while U is enriched in a felsic rock, Cr is enriched in a mafic rock. Furthermore, the changes in the U/Th and Cr/Ti require the oxidation of U and Cr to decouple geochemical behaviors of U relative to Th and Cr relative to Ti. Correlations of  $Fe_{tot}/Ti$  ratios with U/Th and Cr/Ti ratios indicate that dissolved Cr and U species (e.g.,  $CrO_4^{2-}$  and  $UO_2^{2+}$ ) in ocean were adsorbed onto the surface of ferric (hydr)oxides during the formation of iron-rich sediments. These results suggest that a part of shallow ocean was oxygenated -3.2 Gyr, containing oxidized Cr and U species, and that ferric (hydr)oxides were precipitated due to the oxidation of dissolved ferrous iron by molecular oxygen. Therefore, our findings imply that oxygenic photoautotrophs flourished in the photic zone of the 3.2 Gyr ocean.

Keywords: South Africa, hematite, magnetite, chromite