

## **Geochemical Cycling of Fe, S, C, N, Mo in the 3.2 Ga Ocean: Constraints from DXCL-DP black shales**

K.E. YAMAGUCHI<sup>1,2</sup>, Y. KOBAYASHI<sup>1</sup>, A. SHENA<sup>1</sup>, D. KOBAYASHI<sup>1</sup>, S. FUJITA<sup>1</sup>, A. NAGASHIMA<sup>1</sup>, R. SAKAMOTO<sup>3</sup>, H. NARAOKA<sup>3</sup>, Y. YAMAGATA<sup>4</sup>, T. HIRATA<sup>4</sup>, M. IKEHARA<sup>5</sup>, T. ITO<sup>6</sup>, & S. KIYOKAWA<sup>3</sup>

<sup>1</sup>Dept. Chemistry, Toho Univ. (kosei@chem.sci.toho-u.ac.jp)

<sup>2</sup>NASA Astrobiology Inst.

<sup>3</sup>Dept. Earth & Planetary Sciences, Kyushu Univ.

<sup>4</sup>Dept. Earth & Planetary Sciences, Kyoto Univ.

<sup>5</sup>Center for Advanced Marine Core Res., Kochi Univ.

<sup>6</sup>Faculty of Education, Ibaraki Univ.

Coevolution of early life and surface environment has been one of the most important events on Earth. Rise of  $pO_2$  has been widely believed to have occurred at ~2.4 Ga. But geological and geochemical evidence suggest possibility of much earlier existence of oxic atmosphere and oceans. Records of geochemical cycling of bioessential, redox-sensitive elements have keys to decipher mysteries of the co-evolution of Earth and life. Therefore we drilled through Mesoarchean strata in coastal Pilbara (Dixon Island-Cleaverville Drilling Project) in 2007 and 2011, and obtained 3.2 Ga old weathering-free drillcores (CL1, CL2, CL3, DX) of sulfide-rich black shales in the Cleaverville.

We conducted a systematic geochemical study involving sequential extractions of Fe, S, C, and N for phase-dependent contents and their stable isotope compositions by EA-irMS and MC-ICP-MS, in addition to major and trace element analysis by XRF, ICP-AES, and ICP-MS, for >100 samples. Here we integrate our recent investigations into the redox state and nature of microbial biosphere in the 3.2 Ga ocean.

The obtained data are very difficult to explain only by geochemical processes in strictly anoxic environments, where both atmosphere and oceans were completely anoxic, like an environment before the inferred Great Oxidation Event at ~2.4 Ga. Our extensive data set consistently suggests that oxygenic photosynthesis, bacterial sulfate reduction, dissimilatory iron reduction, and microbially mediated redox-cycling of N, possibly involving denitrification and  $N_2$ -fixation, (i.e., modern-style biogeochemical cycling), are very likely to have been already in full function. These may be used as a strong evidence for (at least) local and temporal existence of oxidized environment 3.2 Ga ago. The atmosphere-hydrosphere system 3.2 Ga ago would have been sufficiently oxidized to allow redox-cycling of those elements. Our results have far-reaching and astrobiological implications for earlier evolution of a planetary surface environment.