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Biogeochemical cycling of Fe, S, C, N, and Mo recorded in DXCL black shales suggest existence of oxygenated ocean 3.2 billion years ago

Yamaguchi, K.E.^{1,2}, Naraoka, H.³, Ikehara, M.⁴, Ito, T.⁵, and Kiyokawa, S.³

¹Dept. Chem., Toho Univ. (Funabashi, Japan; kosei@chem.sci.toho-u.ac.jp), ²NASA Astrobiology Inst., ³Dept. Earth Planet. Sci, Kyushu Univ.; ⁴Center for Marine Core Res., Kochi Univ.; ⁵Faculty Edu., Ibaraki Univ.

Rise of atmospheric oxygen, or as known as the Great Oxidation Event (GOE; e.g., [1, 2]), has been widely believed to have occurred at ~2.4 Ga ago. However, geological and geochemical evidence suggest possibility of much earlier existence of oxic atmosphere and oceans. Records of geochemical cycling of bio-essential and redox-sensitive elements have keys to decipher mysteries of the co-evolution of Earth and life. To obtain insight into biogeochemical cycling of those elements and early evolution of microbial biosphere, we drilled through Mesoproterozoic strata in coastal Pilbara (Dixon Island-Cleaverville Drilling Project, [1]), and obtained 3.2 Ga old drillcores (CL1, CL2, and DX) of sulfide-rich black shales in the Cleaverville Group, Pilbara Supergroup [3]. The age of 3.2 Ga is particularly important not only because it is ~800Ma older than the inferred GOE at ~2.4 Ga, but because there is accumulating geochemical evidence for oxygenated atmosphere-ocean system and for diverse microbial biosphere [4, 5, 6, 7, 8].

We conducted a systematic geochemical study involving sequential extractions of Fe, S, C, and N for phase-dependent contents (e.g., pyrite-Fe, reactive-Fe, highly reactive-Fe, unreactive-Fe, pyrite-S, sulfate-S, organic-S, elemental-S, C_{org} , C_{carb} , N_{org} , and N_{clay}) and their stable isotope compositions by EA-IRMS and MC-ICP-MS, in addition to major and trace, redox-sensitive element analysis by XRF, ICP-AES, and ICP-MS, for >100 samples. Here we integrate our investigations into the redox state of ocean and nature of microbial biosphere in the ocean 3.2 Ga ago.

Isotope compositions of C_{org} and S suggest that photosynthetic organisms produced organic matter and sulfate-reducing bacteria were active in a modern Black Sea-type environment with a limited supply of sulfate into the ocean. Nitrogen isotope compositions are fully explained by microbially-mediated redox-cycling of N, possibly involving denitrification (requiring existence of nitrate, the most oxidized form of N) and microbial N_2 -fixation. Relationship between amounts of pyrite-S and C_{org} suggest presence of syngenetic pyrite as well as diagenetic pyrite. Molybdenum concentrations in the samples were moderately high and have positive correlations with C_{org} and S_{py} contents. Iron isotope compositions of the samples are consistent with operation of dissimilatory iron reduction.

All of 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 GOE. Our extensive data set consistently suggests that oxygenic photosynthesis, bacterial sulfate reduction, iron reduction, and microbially mediated redox-cycling of N, possibly involving denitrification and N_2 -fixation, are very likely to have been operating. These may be used as a strong evidence for at least local and temporal existence of oxidized environment as far back as 3.2 Ga ago. The atmosphere-hydrosphere system 3.2 Ga ago would have been sufficiently oxidized to allow redox-cycling of elements during deposition of the sediments, ~800 Ma earlier than commonly thought.

References:

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