

BIOGEOCHEMICAL CYCLING OF IRON, SULFUR, CARBON, NITROGEN, AND MOLYBDENUM IN THE 3.2 GA OCEAN: CONSTRAINTS FROM DXCL-DP BLACK SHALES FROM PILBARA, WESTERN AUSTRALIA.

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Introduction: Co-evolution of early life and surface environment has been one of the most important events on Earth. Rise of atmospheric oxygen, or as known as GOE (Great Oxidation Event: e.g., [1]), has been widely believed to have occurred at around 2.4 billion years ago. But geological and geochemical evidence suggest possibility of much earlier (by hundreds of millions of years) existence of oxic atmosphere and oceans. Records of geochemical cycling of bio-essential, 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 from high-quality samples, 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 [2]. The age of 3.2 Ga is particularly important not only because it is as long as ~800Ma older than the inferred “Great Oxidation Event” when pO_2 was lower than 0.00001 PAL (e.g., [3]) that has been widely believed to have occurred at around 2.4 Ga, but also because there is accumulating geochemical evidence for oxygenated atmosphere-ocean system and for diverse microbial biosphere [4, 5, 6, 7, 8].

Methods: 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, in addition to major and trace (redox-sensitive; e.g., Mo) element analysis by XRF, ICP-AES, and ICP-MS, for >100 samples. Here we integrate our recent investigations into the redox state of ocean and nature of microbial biosphere in the ocean 3.2 Ga ago.

Results and Discussion: Isotope compositions of carbon and sulfur suggest that photosynthetic organisms produced organic matter and sulfate-reducing bacteria were active in a modern Black Sea-type envi-

ronment with a limited supply of sulfate in the 3.2 Ga ocean. Nitrogen isotope compositions are fully explained by microbially-mediated redox-cycling of N, possibly involving denitrification 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 correlation with C_{org} and S_{py} contents.

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, 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. Modern-style biogeochemical cycling of Fe, S, C, N, and Mo has been operating since then. 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. Our suggestions have far-reaching and astrobiological implications for earlier evolution of the surface environment, especially redox state, and marine microbial biosphere.

References:

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