

Sulfur cycling constrained from speciation and isotope analyses of 3.2 Ga black shale recovered by DXCL-DP

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Before the inferred GOE (Great Oxidation Event; Holland 1994) at 2.3-2.4 Ga ago, the surface environment of the Earth could have been, at least locally and/or temporally, slightly oxic as old as 3.2 Ga ago. Such evidence come from a variety of geochemical analysis using the least-metamorphosed 3.2 Ga old drillcores recovered by DXCL-DP (Dixon Island-Cleaverville Drilling Project; Yamaguchi et al., 2009) in northwestern Pilbara region, Western Australia. It includes activity of photosynthetic (oxygen-producing?) organisms (Hosoi et al., 2011), oxidative (nitrate-involving) nitrogen biogeochemical cycling (Yamada et al., 2011) and activity of sulfate-reducing bacteria (Sakamoto et al., 2011).

During biogeochemical cycling of sulfur in sedimentary environment, S-bearing species undergo a variety of biogeochemical reactions and preserved in the sediments as acid-volatile sulfur (AVS), pyrite (FeS₂), sulfate, organic sulfur (S_{org}) and elemental sulfur (S₀). These species, and their S isotope compositions vary depending on various factors such as the redox state of the ocean and microbial activity involved. In this study, we performed S speciation and isotope analyses of the 3.2 Ga old DXCL-DP black shale, in an attempt to constrain the sulfur cycle in the coeval ocean.

Average S contents for each phase was total S = 2.56 wt.%, AVS = 0.02 wt.%, pyrite = 1.61 wt.%, and sulfate = 0.57 wt.%. Pyrite is the most abundant phase. A positive correlation between the pyrite S and organic C, with a slope of 2.2 for the regression line, suggests that the Black Sea type of depositional environment; sulfate-reducing bacteria was active in anaerobic, semi-closed deep water with a limited supply of sulfate overlain by aerobic surface water. The origin of sulfate could have been the oxidation of pyrite on the continents or the oxidation of reduced S-species emanated from submarine hydrothermal activity. Such possibilities can be examined from S isotopic composition of S-bearing species in the samples.

Keywords: Sulfur, speciation, isotope