

Photochemistry of dissolved combined amino acids

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Amino acids are an significant, identifiable portion of the dissolved organic nitrogen pool of natural waters, and are important substrates for microbes at the base of the food web. A portion of the naturally occurring amino acids are photoreactive, which means that photochemistry could play a significant role in the modulation of the microbial utilization of DON. While most research in this area has centered on dissolved free amino acids, most amino acids are present in natural waters as combined amino acids.

The purpose of the present study was to examine the differences in photoreactivity of dissolved free and combined amino acids. Specifically, this work focused on the oxidation of histidine residues in an intact protein (GAPDH) by singlet oxygen.

The results indicate that the reactivity of histidine residues is decreased when in the context of an intact protein, and that the decrease is due to decreased accessibility to the oxidant. The differential reactivity of near-surface and buried residues led to a sensitive method for tracking the intactness of the folded protein during the photolysis.

Return of Archean low sulfate levels during the earliest Mesoproterozoic Oceans

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Sulfate, the second abundant anion in the modern ocean (~28mM), plays an important role in the present biogeochemical cycle of C, S and O. It has been shown that more than 50% of organic matter is remineralized through microbial sulfate reduction and as high as 80% of methane was oxidized by anaerobic methane oxidation archaea coupled with microbial sulfate reduction (Jørgensen, 1982; Valentine, 2002). Furthermore, oceanic sulfate concentration is an important proxy for oxidation state of Precambrian atmosphere and ocean. Therefore unraveling the variation pattern of oceanic sulfate concentration in geological history is very important scientific issue.

A number of studies have shown that oceanic sulfate concentration varied distinctly and periodically in Phanerozoic (e.g., Lowenstein *et al.*, 2003). However, the details of the evolution history of the Precambrian oceanic sulfate concentration are unclear beyond the general increasing trend (Kah *et al.*, 2004). Here we analyzed sulfur isotopic composition of carbonate associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$) and corresponding disseminated pyrite ($\delta^{34}\text{S}_{\text{py}}$) at the 1.6 Ga Gaoyuzhuang Formation in the North China Craton. The results show that both the $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{py}}$ are relatively constant, varying around $13.0\text{‰} \pm 1.8\text{‰}$ and $8.0\text{‰} \pm 2.3\text{‰}$, respectively over 200 m stratigraphic sections. Therefore the sulfur isotopic fractionation ($\Delta^{34}\text{S}$) between the sulfate and pyrite at this time was ~5‰. The relative uniformity in the $\delta^{34}\text{S}_{\text{py}}$ implicates that the pyrite was formed in the water column, and the small $\Delta^{34}\text{S}$ implicates that the sulfate concentration in the earliest Mesoproterozoic ocean would have been extremely low, probably far less than 1 mM. Our identification of extremely low oceanic sulfate concentration in the earliest Mesoproterozoic points to a distinct perturbation in ocean chemistry, which might be related to the decline of coeval atmospheric O_2 concentration.

[1] Jørgensen, B.B. (1982) . *Nature* 296, 643-645. [2] Kah, L.C., Lyons, T.W., and Frank, T.D. (2004) *Nature* 431, 834-838. [3] Lowenstein, T.K., Hardie, L.A., Timofeeff, M.N., and Demicco, R.V. (2003) *Geology* 31, 857-860 [4] Valentine, D.L. (2002) *Antonie van Leeuwenhoek* 81, 271-282.