

The effect of high concentrations of green sulfur bacteria on the biogeochemical carbon cycle of Lago di Cadagno

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In the sulfide rich (meromictic) Lago di Cadagno, primary production is dominated by anoxygenic photosynthesis, and hence serves as a model system for an early prokaryote dominated ocean. Organic matter produced in the anoxic part of the water column by the phototrophic S-bacteria can have large impact on how carbon and sulfur is recycled in the lake. About 50% of the total carbon production of Lago di Cadagno is taking place in the anoxic water. The bacteriochlorophyll *e*-containing green sulfur bacterium *Chlorobium clathratiforme* is the most dominant anoxygenic phototrophic organisms in Lago di Cadagno, making up 95% of the anoxygenic phototrophic population. Here we the effect of high concentrations of green sulfur bacteria on the carbon flow of Lago di Cadagno. We find that green sulfur bacteria had a low mortality both in the photic chemocline and far down in the dark part of the lake leading to a 3.8 times biomass enhancement over a summer. A comparative proteomic study of *C. clathratiforme* show that this organism in the chemocline expresses proteins associated a total phototrophic oxidation of sulfide and thiosulfate to sulfate while fixing carbon using the reverse TCA-cycle. Proteins related to sulfide oxidation were down regulated with depth whereas proteins related to fermentation and reverse TCA-cycle were stable. This could indicate that *C. clathratiforme* at dark might obtain energy by fermentation and hereby get resistant for microbial degradation. Carbon isotope ($\delta^{13}\text{C}$) measurement of particular organic matter in lake water and sediment traps showed moderate (-32‰) depletions reflecting the activity of green sulfur bacteria. Based on the carbon flux measurements in Lake Cadagno we will discuss how high concentrations of phototrophic bacteria can affect the carbon cycle of a Proterozoic sulfide rich ocean.

Evidence of a redox chemocline in post-GOE oceans from the 1.9 Ga Gunflint Iron Formation

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Precambrian banded iron formation (BIF) is a chemical sedimentary rock whose chemistry preserves many aspects of the depositional environment [1]. At ~1.9 Ga in age [2], the Gunflint Iron Formation has the potential to preserve evidence of oxidation of the water column in response to the Great Oxidation Event (GOE). Amphibolite-grade samples were collected along the Gunflint Trail in northern Minnesota, including detailed sampling from an 8-m section of the lower slaty unit, and typically represent a deeper water facies. Unmetamorphosed samples were collected around Thunder Bay, Ontario, and typically represent a shallower water facies, with evidence of silicified microbial mats, hummocky cross-stratification and carbonate-rich BIF being present. Samples show both positive and slightly negative Ce anomalies, ranging from 0.93-1.31 in amphibolite-grade rocks and 1.01-1.86 in relatively unmetamorphosed rocks. Some samples lack a Ce anomaly. In the Phanerozoic fully ventilated ocean, even deep water has a strong negative Ce anomaly. The co-existence of samples with negative and positive Ce anomalies suggests deposition above and below a redox chemocline, supporting the widely held notion that the Paleoproterozoic deep ocean was not ventilated. The composition of chemical sediments may also reflect more local redox conditions and is strongly influenced by post-depositional changes, which suggests that the Ce anomalies may not always be primary [3]. Post-depositional mobility of U can also affect Th/U ratios, however, Pb isotope compositions were used here to infer the true depositional Th/U ratio [4]. Locally oxidized (shallow) water conditions are thus indicated by very large (by comparison with Archean BIF) U/Th and U/Pb ratios and very radiogenic Pb-isotope ratios, supporting preferential U over Th flux in response to oxidative weathering.

- [1] Klein (2005), *Am. Mineral.* **90**, 1473-1499. [2] Fralick *et al.* (2002), *Can. J. Earth Sci.* **39**, 1085-1091. [3] Derry & Jacobsen (1990), *Geochim. Cosmochim. Acta* **54**, 2965-2977. [4] Pollack *et al.* (2009), *Chem. Geol.* **260**, 172-185.