Early evolution of photosynthetic processes before the Great Oxidation: A C and S isotopes perspective

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Six Archaean sedimentary sequences from 3.8 to 2.6Ga have been analysed for carbon and sulphur isotopes in order to determine the evolution of the photosynthesis through the Archaean. Despite obvious signs of metamorphic influences on $\delta^{34}S$ and $\delta^{13}C_{red}$ results from the 3.8Ga (Isua Greenstone Belt) and ~3.3Ga (Barberton Greenstone Belt) formations, it is possible to assess the changes and expansion of the biological activities occuring during this 1Ga period. If there is very little evidence in the Early Archaean at 3.8Ga for photosynthesis, it is clearly present at 3.4/3.2Ga under anoxygenic conditions, in addition to anaerobic activity, with $\delta^{13}C_{red}$ values varying from -34 to -10%. Sulphur isotopes indicate a S-dependent bacterial metabolism. At the dawn of the late Archaean (2.9Ga), the presence of important stromatolitic formations such as Steep Rock Group, Ontario, or the Mushandike Formation, Zimbabwe [1], suggests a dramatic global change in the biological activities. $\delta^{13}C$ records from the carbonate and organic carbon strongly advocate fractionation (~25-29‰) produced by the Rubisco 1 enzyme. This suggests the presence of oxygen and therefore the existence at that time of a flourishing oxygenic photosynthetic process.

The study of well-preserved Late Archaean parts of the Belingwe Greenstone Belt (2.7-2.6Ga), Zimbabwe, shows even more diverse and complex life with a great variety of metabolic processes. Wide ranges of 40% (-23.7 to +16.7%) for δ^{34} S and 36% (-43.8 to -7.0%) for $\delta^{13}C_{red}$ indicate that sulphate reduction, sulphide oxidation, methanogenesis and methanotrophy were active, but dominated by oxygenic and anoxygenic photosynthesis. All these activities were dictacted by the environment, from tidal wave setting to deeper water. Possible bi-products of a methane seep can also be distinguished.

After this 1Ga period of evolution, photosynthetic processes were well-established and seem to have reached almost full operation, interacting in the microbial mat with co-existing metabolic pathways.

[1] Abell P.I., McClory J., Martin A., Nisbet E.G. and Kyser T.K. (1985) *Precambrian Research* **27**, 385-398.

Mercury deposition and flux in Narraguinnep Reservoir, Southwestern Colorado, USA

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The Four Corners area of the southwestern United States has several lakes and reservoirs with Hg advisories recommending limited human consumption of fish as a result of high Hg concentrations in fish. Narraguinnep Reservoir in southwestern Colorado is one such reservoir and is posted with an advisory as Hg in fish tissue exceed the 0.5 µg/g safelevel standard recommended by the State of Colorado. No significant point sources of Hg contamination are known to this reservoir or its supply waters, although several coal-fired power plants in the Four Corners region emit Hg-bearing particulates. Concentrations of Hg were measured in sediment cores collected from Narraguinnep Reservoir to evaluate potential Hg sources and deposition. Reservoir sediment was dated by the 137Cs method and these sediment ages were further refined by relating upstream basin hydrological records with core sedimentology. Rates of Hg flux calculated on the basis of Hg concentrations in the cores, sediment bulk densities, and sedimentation rates increased to an average of 44 ng/cm²/yr after about 1970, which is about a factor of two higher than the Hg flux prior to 1970. In addition, magnetic minerals were separated from core samples and examined petrographically; spherical magnetite particles characteristic of power plant fly ash were present in the post-1970 sediment, but absent in the pre-1970 sediment. The increase in Hg flux corresponds temporally to the construction of several coalfired power plants in the Four Corners region. There are presently 14 coal-fired power plants within 320 km of Narraguinnep Reservoir, which collectively produce about 80,000,000 mega watt hours of power and release about 1,640 kg-Hg/yr through stack emissions. Narraguinnep Reservoir is located about 80 km downwind of two of the largest power plants, which together emit about 950 kg-Hg/year. Temporal patterns of Hg flux and the presence of fly ash magnetite in post-1970 sediment from Narraguinnep Reservoir indicate that the most likely source of Hg to this reservoir is airborne emissions from coal-fired electric power plants, most of which began operation in this region in the late-1960s and early 1970s.