# matters arising

## Early Precambrian oxygen

FEW of the arguments presented by Towe[1] seem strong enough to build up a case against the photosynthetic origin of Precambrian oxygen as defended, for example, by Margulis *et al.*[2]. Note especially that he does not discuss the relative importance of hydrogen escape compared with recombination after water photolysis although it seems to be a critical issue. To the uninformed, however, one argument might seem decisive: the requirement of oxygen for chlorophyll-*a* biosynthesis. If this has been proved absolute it would be difficult not to admit the existence of some free oxygen before the formation of that molecule necessary for oxygen releasing photosynthesis.

Towe has cited Bogorad[3] whose Fig. 1, which summarises chlorophyll-*a* biosynthesis, shows an oxygen-requiring step in the oxidative decarboxylation of coprogen. This is, however, a common step to every porphyrin (haem as well as chlorophylls and bacteriochlorophylls) which in 1966 had essentially been studied with animal mitochondria. In this text (p. 492) it is mentioned that oxygen cannot be universally required for that reaction as it suppresses bacteriochlorophyll production in the purple non-sulphur bacterium *Rhodopseudomonas spheroides*. In a more recent treatment of this subject[4], Bogorad indicated in his Fig. 2 that an alternative to oxygen exists for that step and gives full reference to the work of Tait[5] who showed that photosynthetic bacteria have both aerobic and anaerobic coprogenase activity. Since some blue-green algae are clearly able not only to survive but to sustain abundant growth in anaerobic conditions with photosynthesis based on reduced sulphur like some photosynthetic bacteria[6–8], those species must be equally able to decarboxylate coprogen without oxygen. Towe seems to consider that the anaerobic capacity of blue-green algae favours his hypothesis. I would rather consider that it also agrees with the reverse hypothesis, stating like Brock[9] that "If the bulk of the atmospheric $O_2$ is indeed of biogenic origin, the organisms first involved in $O_2$ formation would of course have developed in an anaerobic environment and would have had to be able to live anaerobically".

The argument that in a reducing atmosphere there would be no selection pressure to tap the immense hydrogen resources of water is unconvincing. What would be the difference between competition for dwindling reductants whether those are consumed by an oxidising atmosphere or prokaryotic photosynthesisers? Anyway even admitting immense resources of $H_2S$ or other reductants which could be used for bacterial photosynthesis, in the competition between organisms, depletion can be a phenomenon localised to some biotic environments.

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TOWE REPLIES—Demoulin is disturbed primarily by my statement[1] that unless the molecular oxygen requirement of chlorophyll-*a* had been a later modification, the evolution of this pigment in an anaerobic early Precambrian environment would have been unfavorable. The ability of some extant blue-green algae to sustain abundant growth in reducing conditions certainly implies that they can make the necessary decarboxylation step without free oxygen. Whether or not such anaerobic decarboxylation of chlorophyll-*a* took place in early Precambrian ancestral forms having photosystem I only, is unknown. But if the sequence data of Schwartz and Dayhoff[2] are correctly interpreted the relevance of this point may be moot. After all, if, as they say, the evolutionary development of aerobic respiration preceded that of photosystem II (and hence oxygenic photosynthesis) the oxygen requirements of chlorophyll-*a* biosynthesis would be of limited significance.

On the other hand, the ability of some modern blue-green algae to thrive in reducing environments while endowed with photosystem II but using photosystem I only[3–5] is certainly not, as Demoulin has asserted also in agreement with the reverse hypothesis; namely, that photosystem II evolved in a reducing environment. The algae in question[3] may survive anaerobic conditions using their photosystem II but they can do so only in the absence of suitable reductants, and tolerance for anaerobic conditions is not the same as dependence on such conditions[6]. There are, it is true, other blue-green algae living today that can grow in a reducing environment[7] but these require photosystem II at all times. Here the exogenous reductants ($H_2S$) keep the $p_{O_2}$ low rather than to act as primary electron donors for photosystem I. Thus it is important to distinguish between not only the different algal metabolisms but also between the effects of an anaerobic environment and those of an anaerobic-reducing environment. The point is that even today in the presence of reducing conditions, water is not the photosynthetic electron donor of choice for those blue-greens able to choose between photosystem I and II[3–5]. There is no such choice for the other modern blue-greens[7] and, of course, no choice was available to any of the early Precambrian ancestors equipped only with photosystem I, energetically unable to take advantage of the hydrogen resource of water regardless of its immensity and ready availability. Thus I emphasised[1] that "only by removal of reduced substances as potential electron donors for photosystem I would there have been significant pressure (to) develop photosystem II".

Certainly, the effectiveness of atmospheric dissociation is important to the early Precambrian environments, and I stated[1] as much, but there are simply too many debatable assumptions involving the solar constant, water vapour mixing ratios, and, especially, hydrogen sources and sinks, implicit in the calculations to make any answer definitive. Photodissociation cannot be ruled out as a likely source of free oxygen in the early Precambrian.

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