

The antiquity of Rubisco

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Rubisco is the most abundant protein on Earth. It is the chief link between carbon in the environment (air and sea) and life.

Rubisco has a complex phylogeny. The green-like Form I rubiscos are characteristic of oxygenic photosynthesis. Rubisco Ib is found in (b)-cyanobacteria and, as a subset of cyanobacteria, plastids in higher plants. Form Ia, also green-like, is used by (a)-cyanobacteria and purple bacteria. Red-like type Id rubisco is used by plastids in red algae. Form II rubiscos are used by a variety of purple bacteria and dinoflagellates. Both Form I and Form II rubiscos have carboxylase activity and are used in the Calvin-Benson cycle. Form III rubisco-like proteins (RLPs) are used by archaea and appear to have carboxylase activity but their function is unknown, while Form IV RLPs may help manage sulphur chemistry.

What geological constraints can be placed on the evolution of the rubiscos? When CO₂ is abundant, rubisco I in cyanobacteria is typically very selective for isotopically light carbon, leaving a strong signature in organic matter ($\delta^{13}\text{C}$ circa -25 to -30 per mil), with carbonates from the concomitant residual reservoir enriched ($\delta^{13}\text{C}$ circa 0 per mil) relative to mantle. Both occur in limestones as old as 3Ga, implying that oxygenic photosynthesis is at least as old as this (a conclusion consistent with biomolecular evidence for Late Archaean cyanobacteria). Form II rubisco, which is simpler (e.g. in *Rhodospirillum rubrum*, may have preceded Form I, if the development of anoxygenic photosynthesis in proteobacteria came before oxygenic photosynthesis. Isotopic evidence suggests though does not prove that this may be as old as 3.5 Ga (Barberton) or even 3.8 Ga (Isua).

Form III RLPs could be derived from a very ancient common ancestor of archaea and bacteria, or there could have been a transfer in either direction between the domains. Rubisco-like proteins may be ancestral to rubisco, predating the modern Calvin-Benson cycle in photosynthesis. Form III RLPs are found in methanogens, which may date back as far as 3.5 Ga or older. Form IV RLPs are of great interest as they occur in anaerobes like *Chlorobium* and in non-photosynthetic *B. subtilis*, where they may act in the methionine salvage pathway (Ashida et al., 2003).

Form I rubiscos exist in aerobic or microaerobic organisms, implying that these conditions were present when the organisms first evolved. This is consistent with the view that local microaerobic conditions (e.g. sulphate) occurred in the late/mid-Archaean. Earlier on, possible hydrogen loss to space may have contributed to an increase on the supply of oxidised species in the surface environment. Just as today the air has coexisting oxygen and methane, so the Archaean surface may at times have had coexisting atmospheric methane with SO₂ in air and sulphate in water. Anaerobic methane oxidation may be very old.