**The Rubisco-Magnesium Affair**

Accounting for half of a leaf’s soluble protein and $10^{11}$ tons of fixated atmospheric CO$_2$ annually (Andersson, 2008), ribulose 1-5-bisphosphate (RuBP) carboxylase (affectionately dubbed ‘rubisco’) is arguably the most important protein on Earth. However, rubisco’s carboxylation of RuBP with inorganic carbon is dependent on scores of delicate factors – essential yet dangerously capricious. Certainly, requiring magnesium (Mg$^{2+}$) ions to function barely eases the biosphere’s peril. However, the Mg$^{2+}$ ion is not an impediment, but a tool – applied correctly, it creates masterpieces from thin air.

Rubisco occurs in four forms, comprised of polymers of two subunits, the catalytic large (50-55kDa) subunit L and the relatively inert small (12-18kDa) subunit S (Andersson, 2008). Form I, the arrangement found in cyanobacteria, algae and metaphyte lineages is a hexadecamer of 8 L subunits sandwiched by 4 S subunits on each side (Andersson, 2008; Taiz and Zeiger 146). Conversely, forms II-IV lack the S subunit and vary widely in L polymerization, being present in dinoflagellates and prokaryotes (Andersson, 2008). Form IV, dubbed rubisco-like proteins (RLPs), lacks many conserved active sites and functions in prokaryotic sulfur metabolism/oxidative stress instead of carbon fixation (Hanson and Tabita, 2001; Taiz and Zeiger 146). Interestingly, this form may represent the evolutionary origin of modern rubisco (Hanson and Tabita, 2001).

After its precipitation from spinach homogenate, rubisco’s carboxylase activity was discovered in 1954 (Wildman and Bonner, 194; Portis and Salvucci, 2005). In a notable study by Arthur Weissbach et al., PGA production was enzymatically assayed with rabbit aldolase and was found to be proportional to the amount of the “carboxylation protein” (Weissbach et al., 1956; Portis and Salvucci, 2005). Surprisingly, rubisco’s oxygenase activity was established almost 15 years later in 1971 – a 1973 study glibly stated that “the oxygenase and carboxylase activities co-purified, and other attempts to separate them were unsuccessful” (Andrews et al., 1973; Portis and Salvucci, 2005). The subsequent years saw much debate on the origins of phosphoglycolate (the product of RuBP oxygenation; relatively useless) and the necessity of transition metal cofactors (Portis and Salvucci, 2005). Understanding of rubisco function was muddled until a 1979 study by Lorimer et al. determined the necessity of an activator $^{4}$CO$_2$ distinct from substrate $^{3}$CO$_2$ (Lorimer et al., 1979; Portis and Salvucci, 2005; Taiz and Zeiger 151). After incubating the enzyme with radiolabelled CO$_2$ and then allowing the enzyme to function in an excess of regular CO$_2$, they found “the observed radiospecific activity of the enzyme was some 40 times that of the unbound CO$_2$ . . . this result can only have occurred if the activator CO$_2$ and the substrate CO$_2$ sites are physically distinct” (Lorimer et al., 1979). The following year, the $^{4}$CO$_2$ was found to carbamylate the ε-amino group of Lys201 at the active sites of rubisco (Lorimer and Miziorko, 1980). Later experiments identified inhibitors of rubisco carbamylation, including the substrate RuBP itself (Jordan and Chollet, 1983; Portis and Salvucci, 2005). These developments lead to the discovery of rubisco activase – an enzyme excising RuBP blocking the $^{4}$CO$_2$ carbamylaition site (Portis and Salvucci, 2005; Taiz and Zeiger 152).

In Lorimer’s 1979 experiment, “no enzyme-bound $^{14}$C was recovered whatsoever when Mg$^{2+}$ was omitted from the elution buffer” (Lorimer et al., 1979). Obviously, the magnesium ion’s importance in rubisco’s function cannot be overstated. Mg$^{2+}$ stabilizes the charged carbamate group of Lys201
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(Lorimer et al., 1979; Lorimer and Miziorko, 1980; Andersson, 2008). Besides the Asp203 and Glu204 ligands controlling charge distribution, the Mg$^{2+}$ ion binds 3 H$_2$O molecules – two being replaced by RuBP, and the last by $^8$CO$_2$ itself (Andersson, 2008). Mg$^{2+}$ is irreplaceable, as “the nature of the divalent metal ion has a profound effect on this efficiency (carboxylation versus oxygenation). Substitution of Mg$^{2+}$ with Mn$^{2+}$ reduces the efficiency of the enzyme some 25-fold” (Lorimer and Pierce, 1989). In effect, all photosynthesis and carbon fixation depends on the Mg$^{2+}$ ion.

Increasing understanding of rubisco has massive implications for humankind. Rubisco is extremely inefficient and prone to oxygenase activity – presenting opportunities for genetic enhancement. Agricultural productivity with an increasing population would directly benefit from improvements to rubisco function. Secondly, as atmospheric CO$_2$ levels rise, heightened rubisco function could play an important role in organically trapping carbon. Nevertheless, whether a ubiquitous workhorse or a fickle liability, rubisco gives all life sustenance.

Works Cited


Lorimer, George H., and Henry M. Miziorko. "Carbamate formation on the epsilon amino group of a lysyl residue as the basis for the activation of ribulose bisphosphate carboxylase by carbon dioxide and magnesium (2+)." *Biochemistry* 19.23 (1980): 5321-5328.


Final word count (excluding in-text citations and references): 600