Part IV

Integrated Modeling of Light and Dark Reactions of Photosynthesis

Chapter 9

Biochemical Model of C$_3$ Photosynthesis

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Summary

A brief overview of the C_3 photosynthesis model described by Graham Farquhar, Susanne von Caemmerer and Joseph Berry is provided. The model was designed to help interpret gas exchange measurements of CO_2 assimilation of leaves and to represent C_3 photosynthesis in other systems such as stomatal control and the CO_2 concentrating function of C_4 photosynthesis. It can predict steady state CO_2 assimilation rates under different environmental conditions of light intensity, temperature, CO_2 and O_2 concentrations. The model is based on Rubisco's kinetic properties and the rate of CO_2 assimilation is given as the minimum of either a Rubisco limited rate, where the substrate ribulose bisphosphate (RuBP) is saturating, or a chloroplast electron transport (or RuBP regeneration) limited rate. The model can be used to estimate in vivo Rubisco activity and chloroplast electron transport capacity. This however requires information on the partial pressure of CO_2 in the chloroplast which has been shown to be less than that in the intercellular airspaces. The temperature dependence of Rubisco kinetic constants is based on both in vitro and in vivo measurements of these parameters. The temperature dependence of the maximum chloroplast electron transport has also been parameterized from both in vivo and in vitro measurements; however the fact that thermal acclimation changes thylakoid properties and the temperature dependence of chloroplast electron transport prevents a unique parameterization. Further studies are required to investigate whether CO_2 assimilation rate at temperature extremes is limited by Rubisco and its activation state or by electron transport capacity in order to improve the model's accuracy under these conditions.

I. Introduction

In this chapter we discuss key attributes of the C_3 photosynthesis model first described by G. Farquhar, S. Von Caemmerer and J. Berry (Berry and Farquhar, 1978; Farquhar et al., 1980; Von Caemmerer and Farquhar, 1981; Farquhar and Von Caemmerer, 1982). This model was designed to help interpret gas exchange measurements of CO_2 assimilation of leaves. It is used to predict steady state CO_2 assimilation rates under different environmental conditions of light intensity, temperature, CO_2 and O_2 partial pressures (pCO_2 and pO_2) and can be embedded in larger models of the global carbon cycle and of land surface feedbacks on climate. It is also frequently used in reverse to predict underlying biochemical properties of leaves from gas exchange measurements (Long and Bernacchi, 2003).

Simplicity is the key to making this type of model useful. This requires careful consideration of the detail that needs to be incorporated and what can safely be left out. It is important to keep the number of parameters that have to be assigned to a minimum. This has been the guiding principle of the design of the model discussed in this chapter and sets it apart from other models that seek to incorporate a larger number of biochemical steps involved in CO_2 assimilation with the purpose of studying regulation of metabolism (Laisk and Oja, 1998; Laisk et al., 2006; Zhu et al., 2007). The model is generally most useful in describing steady state CO_2 assimilation rates, although it has also been incorporated into models describing CO_2 uptake transients during sun flecks (Pearcy et al., 1997).

The model is based on the kinetic properties of ribulose 1,5-bisphosphate carboxylase/ oxygenase (Rubisco, EC 4.1.1.39) and an interesting historical perspective of Rubisco research and discoveries is given by Portis and Parry (2007). The importance of Rubisco in determining the rate of photosynthesis had been inferred early on from correlations between photosynthetic rate and the amount of Rubisco protein in leaves (Björkman, 1968; Wareing et al., 1968; Bowes et al., 1971; Bowes and Ogren, 1972). But perhaps the pivotal event was the discovery that O_2 was a competitive inhibitor of CO_2 fixation, an alternative substrate leading to the side reactions that fuel photorespiration (Bowes et al., 1971; Bowes and Ogren, 1972). This led to the development of photosynthetic models based on Rubisco kinetic properties (Laisk, 1970, 1977; Laing et al., 1974; Peisker, 1974, 1976; Hall and Björkman, 1975). For example, Laing et al.

(1974) and Peisker (1974) showed that a linear dependence of the CO$_2$ compensation point could be explained from Rubisco's kinetic properties. The impact of Rubisco kinetic properties on C$_3$ photosynthesis has been elegantly highlighted in recent studies where the C$_3$-model has been used to characterize Rubisco kinetic properties in transgenic plants expressing mutated Rubisco (Whitney et al., 1999; Whitney and Andrews, 2001; Sharwood et al., 2008).

The model continues to be used almost unchanged from when it was conceived in the late 1970s and early 1980s and it has served as a template for development of other models (Collatz et al., 1991, 1992; Sellers et al., 1996a). The key innovation of this model stemmed from the recognition that losses in coupling between the light dependent reactions and the carbon reactions are minimal. Therefore, the overall rate of photosynthesis could be approximated as the minimum of the potential rates of these processes taken separately (Eq. 9.20). The basis for this efficient coupling is still not well understood (Woodrow and Berry, 1988). Perhaps most surprisingly the equations relating chloroplast electron transport rate to light intensity are still treated empirically in whole leaf models and several different equations are in use (Farquhar et al., 1980; Farquhar and Von Caemmerer, 1982; Farquhar and Wong, 1984; Collatz et al., 1990, 1991, 1992; Long and Bernacchi, 2003). Equations relating ATP production to chloroplast electron transport rate continue to change according to new understanding of the proton requirements of ATP production. Sharkey and co-workers drew attention to a third limitation that may come into play by the rate of triose phosphate export (Sharkey, 1985a; Harley and Sharkey, 1991). There are however several questions that deserve further attention. For example, it is important to know what the CO$_2$ partial pressure (pCO$_2$) is at the site of Rubisco carboxylation and what defines the conductance of CO$_2$ diffusion from intercellular airspace to the chloroplast stroma. This research area is currently receiving considerable attention (Evans and Von Caemmerer, 1996; Terashima et al., 2006; Flexas et al., 2007a, b; Warren, 2007). This question is of particular importance in biotechnological research attempting to redirect photorespiratory CO$_2$ release to the chloroplast (Kebeish et al., 2007) and to attempts at introducing a C$_4$ type CO$_2$ concentrating mechanism into C$_3$ cells where one would like to be able to manipulate CO$_2$ diffusion properties of membranes (Matsuoka et al., 2001; Von Caemmerer, 2003; Mitchell and Sheehy, 2006). Understanding what limits CO$_2$ fixation at extreme temperatures has also become an important question in the endeavor to predict CO$_2$ assimilation rates in these environments. There is at present considerable debate on whether the capacity of chloroplast electron transport to regenerate RuBP or the activation state of Rubisco provide the primary limitation and it is clear that we need a better understanding how Rubisco activation state is modulated by environmental variables (Weis and Berry, 1988; Crafts-Brandner and Salvucci, 2000; Wise et al., 2004; Cen and Sage, 2005; Yamori et al., 2005, 2006b, 2008).

The photosynthesis model described here provides a set of hypotheses brought together in a quantitative form that can be used as a research tool to design and interpret both field and laboratory based experiments. Both the current availability of transgenic plants with biochemical impairments and the range of Arabidopsis knockout mutants and the interest in improving CO$_2$ assimilation rates through genetic manipulation are providing interesting new tests and applications for modeling photosynthesis (Von Caemmerer, 2000, 2003; Raines, 2003, 2006). Newer portable gas exchange systems have opened up opportunities for ecophysiological studies (Björkman et al., 1972; Ellsworth et al., 2004; Wright et al., 2004).

II. The Rate Equations of CO$_2$ Assimilation

Farquhar et al. (1980) showed that CO$_2$ assimilation rate A was given by

$$A = V_c - 0.5V_o - R_d, \qquad (9.1)$$

where A denotes net CO$_2$ assimilation rate, V_c and V_o are the carboxylase and oxygenase rates of Rubisco and R_d denotes day respiration, which comprises mitochondrial CO$_2$ release occurring in the light other than that of photorespiration. Equation (9.1) can be rewritten in a simpler

form as:

$$A = V_c \left(1 - 0.5\phi\right) - R_d, \qquad (9.2)$$

where ϕ is the ratio of oxygenation to carboxylation rates, V_o/V_c. Rubisco, located in the chloroplast stroma, catalyses the competing reactions of the carboxylation and the oxygenation of ribulose bisphosphate (Andrews and Lorimer, 1987). The carboxylation of RuBP is the first step of the photosynthetic carbon reduction (PCR) cycle and the carboxylation of 1 mol of RuBP leads to the formation of 2 mols of phosphoglycerate (PGA). The oxygenation of 1 mol of RuBP on the other hand leads to the formation of 1 mol of PGA and 1 mol of phosphoglycolate (PGly). We assume that the recycling of 1 mol of PGly in the photorespiratory carbon oxidation (PCO) cycle results in the release of 0.5 mol of CO_2 in the mitochondria (Fig. 9.1). It has been suggested that the release may be less than 0.5 and there continue to be reports of complete oxidation of glycolate as proposed by Israel Zelitch (Hanson and Peterson, 1986; Zelitch, 1989; Harley and Sharkey, 1991).

The ratio of oxygenation to carboxylation rate, ϕ, is determined solely by the kinetic constants of Rubisco:

$$\phi = \frac{V_o}{V_c} = \left(\frac{1}{S_{c/o}}\right)\frac{O}{C} = \left(\frac{V_{o\,max}}{K_o}\frac{K_c}{V_{c\,max}}\right)\frac{O}{C}, \qquad (9.3)$$

where $S_{c/o}$ is the relative specificity of Rubisco and C and O are the chloroplastic pCO_2 and pO_2; V_{cmax}, V_{omax}, K_c and K_o are the maximal rates and the Michaelis–Menten constants of carboxylation and oxygenation, respectively.

Inspection of Eq. (9.2) shows that when $R_d = 0$, $A = 0$ when $\phi = 2$. The chloroplast pCO_2 at which this occurs has been named Γ^* (Laisk, 1977; Laisk and Oja, 1998) and from the above equation it follows that

$$\Gamma^* = \frac{0.5O}{S_{c/o}} = \gamma^* O \qquad (9.4)$$

and

$$\phi = \frac{2\Gamma^*}{C}. \qquad (9.5)$$

Substituting this into Eq. (9.2) one can show that

$$A = \left(1 - \Gamma^*/C\right)V_c - R_d. \qquad (9.6)$$

It is assumed that some mitochondrial respiration (R_d) continues in the light although not necessarily at the rate that occurs in the dark (Brooks and Farquhar, 1985; Atkin et al., 1998; Hoefnagel et al., 1998). It has also been suggested that the rate of day respiration may depend on the rate of photorespiration (Bykova et al., 2005; Tcherkez et al., 2008). If this were indeed the case and the two were related in a predictable way then Eqs. (9.1), (9.2), (9.6) would need to be modified to reflect this.

The rate of photorespiration (V_{phr}) is half the rate of oxygenation and is given by $(\Gamma^*/C)V_c$ and can be calculated from gas exchange measurements by the following equation:

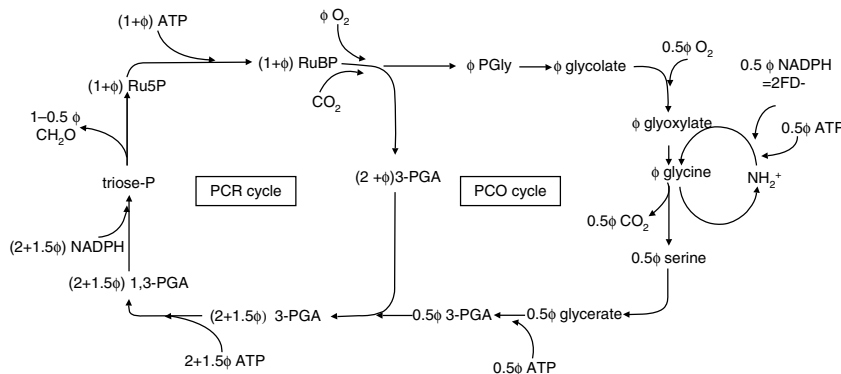$$V_{phr} = \frac{\Gamma^*}{C - \Gamma^*}\left(A + R_d\right). \qquad (9.7)$$

Fig. 9.1. Stoichiometry of the photosynthetic carbon reduction (PCR) cycle and photorespiratory carbon oxidation (PCO) cycle (ϕ denotes the ratio of Rubisco oxygenation to carboxylation)

The basis of the Rubisco limited part of the model is given by Eqs. (9.1)–(9.3). To complete this part of the model the dependencies of Rubisco velocity on pCO_2, pO_2, irradiance and temperature need to be added. Rubisco occurs at high concentration in the chloroplast stroma relative to the Michaelis–Menten constant for its substrate RuBP and it was the special kinetics that apply under these conditions that allowed the simple binary formulation of CO_2 assimilation rate as being either RuBP saturated, or limited by the rate of RuBP regeneration (Berry and Farquhar, 1978; Collatz, 1978; Farquhar, 1979; Farquhar et al., 1980; Farquhar and Von Caemmerer, 1982; Collatz et al., 1990).

A. RuBP Saturated (or Rubisco Limited) CO$_2$ Assimilation Rate

Since O_2 inhibits RuBP carboxylation competitively with respect to CO_2, the RuBP saturated carboxylation rate is given by

$$W_c = \frac{C V_{c\,max}}{C + K_c \left(1 + O/K_o\right)}, \qquad (9.8)$$

(Bowes and Ogren, 1972; Badger and Andrews, 1974). Using Eq. (9.8) to substitute for V_c in Eq. (9.6) yields an expression for the RuBP saturated rate of CO_2 assimilation,

$$A_c = \frac{(C - \Gamma^*) V_{c\,max}}{C + K_c \left(1 + O/K_o\right)} - R_d. \qquad (9.9)$$

Because of its dependence on the maximum Rubisco activity (V_{cmax}), A_c is also often called the Rubisco limited rate of CO_2 assimilation.

The Rubisco limited rate of CO_2 assimilation suggests that the dependence of CO_2 assimilation on pCO_2 should have a Michaelis–Menten form. However as noted by several researchers (Laisk and Oja, 1974; Lilley and Walker, 1975; Ku and Edwards, 1977) CO_2 assimilation rate saturates more quickly than can be predicted from the RuBP saturated CO_2 assimilation rate alone. This can be seen in the example of a CO_2 response curve for CO_2 assimilation rate of a tobacco leaf (Fig. 9.2). In the leaf of a transgenic tobacco with an antisense construct to the small subunit of Rubisco the amount of Rubisco per leaf area has been reduced with little alteration to other chloroplast components. In this case the rate of
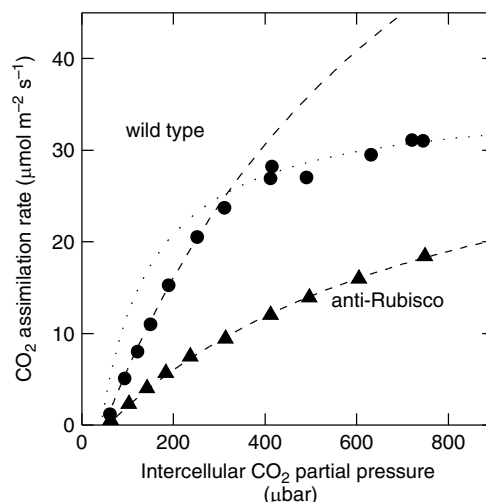

Fig. 9.2. CO_2 assimilation rate, A, as a function of intercellular pCO_2 for a leaf of a wild type ($\bullet$) and transgenic tobacco with reduced amount of Rubisco ($\blacktriangle$). Measurements were made at an irradiance of $1,000\,\mu$mol quanta $m^{-2}\,s^{-1}$ and a leaf temperature of $25\,°C$. The dashed lines are A predicted from the Rubisco limited rate (Eq. 9.9). The dotted line is A predicted from the RuBP regeneration (electron transport) limited rate (adapted from Von Caemmerer et al., 1994)

CO_2 assimilation can be modeled solely by the Rubisco limited rate.

B. RuBP Regeneration Limited (or Electron Transport Limited) CO$_2$ Assimilation Rate

The synthesis of RuBP requires energy in the form of NADPH and ATP and the rate of the Rubisco reaction may become limited by the supply of RuBP. Farquhar (1979) showed that the partitioning of RuBP to carboxylation and oxygenation follows the same kinetics (Eq. 9.3) under limiting RuBP supply. The consumption rates of ATP and NADPH required to regenerate RuBP at the rate of $(1 + \phi)V_c$ were derived from the stoichiometries given in Fig. 9.1. Summing the requirements,

$$\text{the rate of NADPH consumption} = (2 + 2\phi)V_c \qquad (9.10)$$

and

$$\text{the rate of ATP consumption} = (3 + 3.5\phi)V_c \qquad (9.11)$$

(Berry and Farquhar, 1978; Farquhar et al., 1980; Farquhar and Von Caemmerer, 1982; Von Caemmerer, 2000).

The reduction of $NADP^+$ to $NADPH + H^+$ requires the transfer of two electrons through the whole electron transport chain. The rate of whole chain electron transport, required to regenerate RuBP can be calculated from the rate of NADPH consumption (Eq. 9.10) as:

$$(4 + 4\phi)V_c = (4 + 8\Gamma^*/C)V_c \qquad (9.12)$$

and the electron transport limited rate of RuBP regeneration is given by

$$W_j = \frac{J}{(4 + 8\Gamma^*/C)}, \qquad (9.13)$$

where J is the potential electron transport rate, which depends on irradiance.

Light driven electron transport is coupled to the transfer of protons across the thylakoid membrane into the lumen, but neither the stoichiometry of the H^+/e^- ratio or the number of protons required to generate one ATP are known with certainty and may well be flexible. We therefore use the NADPH limited expressions in this chapter. For a more detailed discussion on the formulation for an ATP limited rate of electron transport see Von Caemmerer (2000) or Yin et al. (2004) and Chapter 11 by Xinyou Yin, Jeremy Harbinson and Paul Struik of this book.

Substituting W_j for V_c in Eq. (9.6) yields an expression for the RuBP regeneration (or electron transport) limited rate of CO_2 assimilation:

$$A_j = \frac{(C - \Gamma^*)J}{4C + 8\Gamma^*} - R_d. \qquad (9.14)$$

The CO_2 dependence of A_j is shown in Fig. 9.2 by the dotted line. Here the assumption is made that chloroplast electron transport rate is limiting the rate of RuBP regeneration rather than the enzymes involved in the regeneration of RuBP such as FBPase or SBPase. Studies with transgenic tobacco plants with antisense reductions in the content of chloroplast cytochrome bf complex show a close linear relationship between the cytochrome b_6f content and CO_2 assimilation rate, in support of this hypothesis (Price et al., 1995, 1998; Ruuska et al., 2000a; Baroli et al., 2008) and an example is shown in Fig. 9.3. Studies with
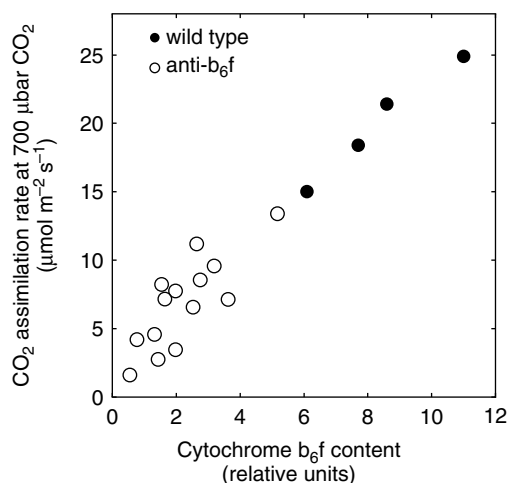

Fig. 9.3. CO_2 assimilation rate versus chloroplast cytochrome b_6f content in wild type and transgenic tobacco with an antisense construct against the Rieske FeS protein of the chloroplast cytochrome b_6f complex. Gas exchange measurements were made at $1{,}000\,\mu$mol quanta $m^{-2}\,s^{-1}$, $700\,\mu$bar CO_2 and a leaf temperature of $25\,°C$ (data from Ruuska et al., 2000a)

transgenic plants with reductions in GAPDH, FBPase, SBPase, and phosphoribulokinase have also confirmed that assuming an electron transport limitation is a reasonable assumption under most circumstances (Stitt and Sonnewald, 1995; Raines, 2003). However there are also some studies that show enhanced CO_2 assimilation rates in transgenic plants overexpressing SBPase (Miyagawa et al., 2001; Lefebvre et al., 2005; Feng et al., 2007; Chapter 15 of this book by Ian E. Woodrow). It is possible to write expressions for limitations of CO_2 assimilation rate by any of the enzymes involved in RuBP regeneration following the stoichiometries given by Farquhar and Von Caemmerer (1982), Brooks and Farquhar (1985) and Von Caemmerer (2000). It is important to note that if these reactions were limiting CO_2 assimilation rate the CO_2 dependence would be different to that if electron transport limited the rate.

C. Light Intensity Dependence of Electron Transport Rate

At present the following empirical equation (Farquhar and Wong, 1984) is used to link potential electron transport rate, J, to irradiance:

$$\theta J^2 - J(I_2 + J_{\max}) + I_2 J_{\max} = 0, \qquad (9.15)$$

where I_2 is the useful light absorbed by PS II and $J_{\max}$ is the maximum electron transport rate and θ is an empirical curvature factor (0.7 is a good average value, Evans, 1989). I_2 is related to incident irradiance I by

$$I_2 = I \cdot abs \cdot (1 - f)/2. \qquad (9.16)$$

In sunlight the absorptance (*abs*) of leaves is commonly about 0.85 and f is to correct for spectral quality of the light ($f \sim 0.15$, Evans, 1987). Ögren and Evans (1993) give a detailed discussion of the parameters of Eq. (9.16). The denominator 2 is because we assume half the light absorbed needs to reach each photosystem. The equation can be solved for J as follows

$$J = \frac{I_2 + J_{\max} - \sqrt{(I_2 + J_{\max})^2 - 4\theta I_2 J_{\max}}}{2\theta}.$$
$$(9.17)$$

This equation is a non-rectangular hyperbola with a smooth transition from light limitation ($J = I_2$) to light saturation ($J = J_{\max}$), where $J_{\max}$ is an upper limit to potential chloroplast electron transport determined by the components of the chloroplast electron transport chain. Support for this hypothesis of a limitation on the maximum capacity for RuBP regeneration is shown in Fig. 9.3 where CO$_2$ assimilation rate measured at high pCO$_2$ and high irradiance is correlated with the amount of cytochrome b$_6$f content in tobacco plants were cytochrome b$_6$f content has been reduced via antisense techniques (Price et al., 1998; Ruuska et al., 2000a; Baroli et al., 2008).

D. Export Limited CO$_2$ *Assimilation Rate*

At high CO$_2$ partial pressure, particularly in combination with high irradiance, or low O$_2$ partial pressure or at low temperatures, the rate of CO$_2$ assimilation can sometimes be limited by the rate at which triose phosphates are utilized in the synthesis of starch and sucrose. Then

$$W_p = 3T_p / (1 - \Gamma^* / C) \qquad (9.18)$$

and CO$_2$ assimilation rate is given by

$$A_p = 3T_p - R_d, \qquad (9.19)$$

where T_p is the rate of inorganic phosphate supply to the chloroplast, and equal to the triose phosphate export from the chloroplast (Farquhar and Von Caemmerer, 1982; Sharkey, 1985b; Harley and Sharkey, 1991). Under these conditions A is insensitive to changes in CO$_2$ and O$_2$ partial pressure. For a detailed discussion see Harley and Sharkey (1991).

E. Summary of Rate Equations

Equations (9.8), (9.13), (9.18) describe the basic C$_3$ model with

$$A = (1 - \Gamma^* / C) \cdot \min\{W_c, W_j, W_p\} - R_d,$$
$$(9.20)$$

or using Eqs. (9.9), (9.14), (9.19)

$$A = \min\{A_c, A_j, A_p\}, \qquad (9.21)$$

when $C > \Gamma^*$. This is illustrated in Fig. 9.2 for wild type tobacco where the solid line shows the actual rate of CO$_2$ assimilation and the dashed line is the Rubisco limited rate A_c, and the dotted line is the electron transport limited rate A_j. A phosphate limitation rate for A_p is not shown in this example (but see Von Caemmerer, 2000; Long and Bernacchi, 2003; Chapter 10 of this book by Carl J. Bernacchi, David Rosenthal, Carlos Pimentel, Stephen P. Long and Graham D. Farquhar).

In this form the model has discontinuities at the transitions between the different limitations. This can provide mathematical problems when the model is used as a submodel in other applications. The discontinuities can be smoothed using quadratic expressions (Kirschbaum and Farquhar, 1984; Collatz et al., 1991).

III. Parameters and their Temperature Dependencies

Depending on the application of the model most of the parameter values can be assigned a priori leaving only V_{cmax} and $J_{\max}$ and g_i (the conductance to CO$_2$ diffusion from intercellular airspace to the chloroplast, discussed in the next section) to be assigned anew.

A. Rubisco Kinetic Constants

Kinetic constants of Rubisco are similar amongst C_3 species and it is common to use the same K_c, K_o, and $S_{c/o}$ for all higher plant C_3 species. There are however reports of variation of Rubisco kinetic parameters which may need to be considered in some applications of the model, although very few complete data sets exist at present (Sage, 2002; Galmes et al., 2005; Tcherkez et al., 2006; Kubien et al., 2008). Farquhar et al. (1980) used constants derived from in vitro measurements by Badger and co-workers. Von Caemmerer et al. (1994) used transgenic tobacco with reduced amounts of Rubisco to determine Rubisco kinetic constants in vivo at 25°C (Table 9.1). These values were in good agreement with in vitro measurements made in tobacco (Whitney et al., 1999). Brooks and Farquhar (1985) measured Γ^* as a function of temperature and found that spinach had a slightly higher value than wheat, a result borne out by subsequent specificity measurements in vitro (Kane et al., 1994). It is important to note that $S_{c/o}$, K_c and K_o are linked (Eq. 9.3) to assure consistency when assigning values.

The maximum rate V_{cmax} is dependent on the amount and the activation state of Rubisco protein present in the leaf and will vary from leaf to leaf. Rubisco has a molecular weight of 550 kDa and eight catalytic sites per molecule. To be catalytically competent Rubisco's sites must be activated. This requires the carbamylation of a lysine residue within the catalytic site to allow the binding of a Mg^{2+} (rev. Andrews and Lorimer, 1987). In C_3 species Rubiso has a catalytic turnover rate of approximately 3.5 s^{-1} per site and thus 1 g m^{-2} of Rubisco has a V_{cmax} of 51 µmol m^{-2} s^{-1} when all sites are carbamylated.

It was shown early on with the first gas exchange measurements that the temperature dependencies of Rubisco's carboxylation and oxygenation rates are reflected in the temperature dependency of the CO_2 assimilation rates of leaves (Björkman and Pearcy, 1971; Björkman et al., 1980). The need for accurate estimates of the temperature dependencies of Rubisco kinetic parameters has become more urgent as mathematical modelers try to predict the impact of increasing global CO_2 concentrations and temperatures (Bowes, 1991; Long, 1991; McMurtrie and Wang, 1993; Whitehead et al., 2001; Medlyn et al., 2002; Lloyd and Farquhar, 2008). The temperature dependence of the kinetic constants can be described by an Arrhenius function of the form

$$Parameter(T) = Parameter(25^o C)$$
$$\times \exp\left[(t-25)\,E\big/(298R\,(273+t))\right], \quad (9.22)$$

where R (8.31 J K^{-1} mol^{-1}) is the universal gas constant and t is temperature in °C (Badger and Collatz, 1977). Using the Arrhenius function to describe temperature dependencies of the photosynthetic processes is a semi empirical approach, but allows for easy comparison between studies. The Q_{10} function has also been used to approximate the temperature dependence of these kinetic constants (Woodrow and Berry, 1988). Table 2.2 in Von Caemmerer (2000) provides a comparison of experimental measurements of the in vitro temperature dependencies of Rubisco kinetic constants. Temperature dependencies were also reviewed by (Medlyn et al., 2002). Bernacchi and co workers using a similar approach to Von Caemmerer et al. (1994) determined the temperature dependence of Γ^*, K_c and K_o in vivo in transgenic tobacco with reduced amounts of Rubisco (Bernacchi et al., 2001, 2002; Chapter 10) and these are shown in Table 9.1. They are surprisingly similar to the initial temperature dependencies used by Farquhar et al. (1980), except that K_c has a greater apparent activation energy.

Table 9.1. Photosynthetic parameters at 25 °C and their activation energies E

Parameter	Value	E (kJ mol^{-1})
K_c (µbar)	260[a](267)[b]	59.36[c](80.99)[b]
K_o (mbar)	179[a](164)	35.94 (23.72)
$S_{c/o}$ (mol/mol)	97.5[a]	
$S_{c/o}$ (bar/bar)	2,585	
γ^* (bar/bar) (0.5/$S_{c/o}$)	0.0001935	23.4
Γ^* (µbar CO_2, 200 mbar O_2)	38.6[a](36.9)	23.4 (24.6)
V_{cmax} (µmol m^{-2} s^{-1})	80[d]	58.52
R_d (µmol m^{-2} s^{-1})	1[d]	66.4
J_{max} (µmol m^{-2} s^{-1})	160[d]	37
H (kJ mol^{-1})	220	
S (J K^{-1} mol^{-1})	710	

[a] (Von Caemmerer et al., 1994)
[b] Numbers in brackets are taken from Bernacchi et al. (2002) assuming an average atmospheric pressure of 987 mbar in Urbana Illinois
[c] Activation energies used by Farquhar et al. (1980)
[d] Varies dependent on photosynthetic capacity of the leaf

Throughout this chapter, the values of chloroplastic CO$_2$ and O$_2$, K_c and K_o are given in units of partial pressure. The chemical activity of a dissolved gas is proportional to its gas phase (vapor) pressure and thus the partial pressure of a gas existing in equilibrium with that in solution is a better measure of its chemical activity than dissolved concentrations (Badger and Collatz, 1977). The main difference between the use of gas phase units of partial pressure and that of dissolved concentrations (μM) arises when temperature dependencies are considered. If dissolved concentrations are used the temperature dependencies of the solubility of the dissolved gas need to be considered.

B. Parameterization of Chloroplast Electron Transport Rate

To parameterize the RuBP regeneration limited rate of CO$_2$ assimilation, Γ^* and the light dependence of potential electron transport rate need to be considered (Eq. 9.15). Values of absorptance and the curvature factor θ have only a very small temperature dependence and can be assigned a priori with the values given in Eqs. (9.15), (9.16) (Bernacchi et al., 2003). The only parameter that needs to be newly assigned is the maximum electron transport rate J_{max}. We assume that J_{max} depends on the amount of thylakoid components such as the cytochrome b$_6$f complex for example and is dependent on the amount of thylakoid protein present (Fig. 9.3). J_{max} is given in μmol e$^-$ m^{-2} s^{-1} and the ratio of J_{max} to V_{cmax} is usually between at 1.5–2 at 25 °C (Wullschleger, 1993; de Pury and Farquhar, 1997).

The dependence of J_{max} on temperature has been estimated in vitro with isolated thylakoids (Armond et al., 1978; Björkman et al., 1980; Sage et al., 1995; Cen and Sage, 2005; Yamori et al., 2008). Farquhar et al. (1980) used the data of Nolan and Smillie (1976) to determine the parameters E, S, H in the following empirical expression:

$$J_{max} = J_{max}\left(25^oC\right)\exp\left(\frac{(T-298)\,E}{298RT}\right)$$
$$*\frac{\left[1+\exp\left(\frac{298S-H}{298R}\right)\right]}{\left[1+\exp\left(\frac{ST-H}{RT}\right)\right]}, \qquad (9.23)$$
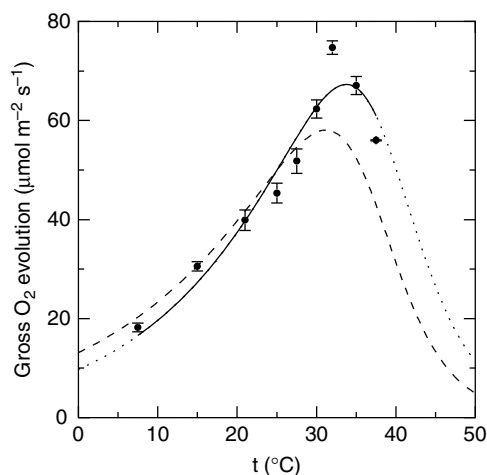

Fig. 9.4. Gross O$_2$ evolution as a function leaf temperature measured on leaf discs of tobacco as ^{16}O$_2$ evolution at 1,700 μmol quanta m^{-2} s^{-1}, 1.5% CO$_2$. Measurements were made as described by Ruuska et al. (2000b) and data are redrawn from Badger et al. (2000). The data were fitted with Eqs. (9.23) and (9.24) and $E = 44.72$ kJ mol^{-1}, $H = 210$ kJ mol^{-1}, $S = 673$ J K^{-1} mol^{-1} and gross O$_2$ evolution of 50 μmol m^{-2} s^{-1} at 25 °C. These measurements and the fit are compared with the temperature dependence of J_{max} (Eq. 9.23) used by Farquhar et al. (1980), expressed here as gross O$_2$ evolution normalized to the value at 25 °C. Parameters are given in Table 9.1

where T is in °K. This equation is shown in Fig. 9.4 with parameters listed in Table 9.1. The parameters S and H are the entropy and enthalpy of a hypothetical equilibrium between an active and inactive form of the limiting component of electron transport, E is the apparent activation energy for low temperature limited electron transport. Discussions on the origins of Eq. (9.23) can be found in several publications (Tenhunen et al., 1976; Hall, 1979; Farquhar et al., 1980; Von Caemmerer, 2000; Medlyn et al., 2002). Acclimation of the thylakoid membrane can occur when plants are grown at different temperatures, shifting the temperature optimum (Berry and Björkman, 1980; Björkman et al., 1980; Sage et al., 1995; Yamori et al., 2008). It is therefore useful to have an equation for the temperature optimum:

$$T_{opt} = H\left[S + R\ln\left(H/E - 1\right)\right]. \qquad (9.24)$$

Equations (9.23) and (9.24) can be used together to fit temperature response curves of in vivo or in vitro measurements of electron transport rate.

An example of measurements of actual electron transport rate is shown in Fig. 9.4. In this case the actual electron transport rate was measured as $^{16}O_2$ evolution at high pCO_2 and high light intensity in tobacco leaf discs (Badger et al., 2000; Ruuska et al., 2000b). Other temperature dependencies have been given using empirical fitting functions (Kirschbaum and Farquhar, 1984; Bernacchi et al., 2003; June et al., 2004; Yamori et al., 2008). It needs to be borne in mind that many of the temperature dependencies derived for J_{max} in vitro may not represent true temperature dependencies of maximal electron transport rate in vivo as downstream reactions in carbon metabolism can exert feedback inhibition on electron transport (Woodrow and Berry, 1988). There is concern that the steep decline in J_{max} at high temperature may be an artifact of the in vitro measuring system. However, Yamori et al. (2008) compared the temperature dependence of J_{max} estimated in vivo from measurements of CO_2 assimilation rate at high CO_2 with in vitro measurements and found close agreement over a wide temperature range except at the lowest and highest temperatures. Bernacchi et al. (2003) found that J estimated from gas exchange could be fitted with a simple exponential function and did not saturate in high temperature grown tobacco. A simpler empirical form was introduced by June et al. (2004):

$$J\left(t_{L}\right) = J(t_{o})e^{-\left(\frac{t_{L}-t_{o}}{\Omega}\right)^{2}}, \qquad (9.25)$$

where t_L is the leaf temperature (°C), $J(t_o)$ is the rate of electron transport at the optimum temperature t_o, and Ω is the difference in temperature from t_o at which J falls to e^{-1} (0.37) of its value at t_o.

IV. The Role of Rubisco Activation State

One of the concerns in modeling Rubisco limited CO_2 assimilation rate is if and how to incorporate a function for the variation of Rubisco activation state. To function, Rubisco's catalytic sites must be activated through the reversible carbamylation of a lysine residue within the site, followed by the rapid binding of an essential Mg^{2+} (Andrews and Lorimer, 1987). It is possible to measure both Rubisco activity and the carbamylation state of Rubisco in leaf extracts (Butz and Sharkey, 1989). In vitro studies of Rubisco activation kinetics suggest that the equilibrium carbamylation in the absence of RuBP would be less than 25% at the pH, Mg^{2+}, and CO_2 concentrations thought to occur in the chloroplast (Lorimer et al., 1976). Furthermore, when RuBP was present in vitro assays, it appeared to block carbamylation by binding tightly to non-carbamylated sites (Jordan and Chollet, 1983). These in vitro difficulties in Rubisco carbamylation are eliminated in vivo by the presence of a second protein, Rubisco activase (Portis, 2003). Activase requires ATP hydrolysis to function and removes sugar phosphates from carbamylated and uncarbamylated Rubisco sites, thereby promoting carbamylation (Andrews et al., 1995; Portis, 2003). In vivo Rubisco activation state has been shown to vary with irradiance, temperature and pCO_2 (Von Caemmerer and Quick, 2000; Weis and Berry, 1988; Salvucci and Crafts-Brandner, 2004a). Although Rubisco is frequently observed to be fully active at high irradiance, ambient pCO_2 and moderate temperatures (Von Caemmerer and Edmondson, 1986) its activation state can decline steeply at high temperature (Weis and Berry, 1988; Crafts-Brandner and Salvucci, 2000; Cen and Sage, 2005; Yamori et al., 2006b).

A. Variation of Rubisco Activation with Light and pCO_2

Von Caemmerer (2000) reviewed the role Rubisco activation state may play in modeling C_3 photosynthesis with variation in irradiance and pCO_2. At low pCO_2 Rubisco can be almost fully carbamylated even at low light whereas it declines at high pCO_2 (Sage et al., 1990; Von Caemmerer and Quick, 2000). Sage (1990) therefore suggested that Rubisco's activation state was lowered only under conditions where RuBP regeneration rate was limiting CO_2 assimilation rate. If this is the case Rubisco activation state would not need to be introduced as a separate variable into the model equations. There is some support for this hypothesis in gas exchange measurements which show that the initial slope of the CO_2 response curve is frequently independent of irradiance down to quite low irradiance levels (Brooks and Farquhar, 1985; Evans, 1986; Sage et al., 1990). At low pCO_2 the capacity for RuBP

regeneration exceeds the carboxylation capacity and presumably the transthylakoid ΔpH as well as the ATP/ADP ratio are likely to be high, which in turn may translate into a greater activase activity. In the same vein, the carbamylation state was found to be high at low irradiance and ambient pCO_2 in transgenic tobacco plants with reduced amount of Rubisco compared to wild type plants (Quick et al., 1991), whereas transgenic tobacco with reduced cytochrome b$_6$f content had reduced carbamylation levels compared to wild type (Price et al., 1998; Ruuska et al., 2000a). The complex dependence of activation on pCO_2 and irradiance illustrates that Rubisco carbamylation is no simple function of irradiance. The results with transgenic plants suggest some interaction between Rubisco activation state and the balance between potential electron transport rate and Rubisco carboxylation rate as had been suggested by Sage (1990).

B. Variation of Rubisco Activation with Temperature

Experiments with a variety of species have established that Rubisco activation state declines with increasing temperature at ambient pCO_2 (Weis, 1981; Weis and Berry, 1988; Feller et al., 1998; Crafts-Brandner and Salvucci, 2000; Haldimann and Feller, 2004, 2005; Salvucci and Crafts-Brandner, 2004a; Yamori et al., 2006b). It is thought that Rubisco is inactivated at high temperature due to heat induced inactivation of Rubisco activase which regulates Rubisco activation state (Salvucci and Crafts-Brandner, 2004a, b). Cen and Sage (2005), who examined the interaction of pCO_2 and temperature on Rubisco activation in sweet potato, found Rubisco activation states to be greater at low compared to high pCO_2 at all temperature. There is at the moment no complete information on how temperature, pCO_2 and irradiance interact to modulate Rubisco activation and clearly more research is required to establish the underlying mechanisms. If both Rubisco activation and electron transport are reduced as was suggested by the study of Yamori et al. (2006b) then Rubisco activation state may need to be introduced as an extra variable in Eqs. (9.8) and (9.9). Sellers et al. (1996a) introduced the following

equation for Rubisco activation as a function of leaf temperature:

$$a_R = 1 / \left(1 + e^{0.3(T_l - S_2)}\right), \qquad (9.26)$$

where a_R is the fraction of Rubisco that is active and S_2 is a temperature at which half of the Rubisco is inactive. S_2 varies from 303 K for needle leaf conifers to 313 K for tropical evergreen trees (Table 5 in Sellers et al., 1996b). This equation has similar properties to Eq. (9.23) and can be applied equally well to J_{max}. There is little empirical difference between assuming that J_{max} or Rubisco activation limits photosynthesis at high temperature and ambient pCO_2 since both activities have similar sensitivity to temperature, but there may be subtle differences in the simulated response under low or high pCO_2 conditions. The models of Collatz et al. (1991) and Sellers et al. (1996a) assume that Rubisco activation is most limiting.

V. Estimating Chloroplast pCO_2

To examine the biochemistry of photosynthesis in leaves ideally one would like to measure CO_2 assimilation rate in relation to chloroplast CO_2 partial pressures, as this is the CO_2 pressure determining the Rubisco carboxylation. It is common practice to calculate the CO_2 partial pressure in the sub-stomatal cavities (referred to as intercellular CO_2 partial pressure) from water vapor exchange measurements. This eliminates an important variability, as stomatal conductance varies as stomata themselves respond to CO_2 and irradiance and this has become a standard reference CO_2 (Von Caemmerer and Farquhar, 1981). However measurements of carbon isotope discrimination concurrently with gas exchange measurements have shown that there is a substantial drop in pCO_2 from intercellular airspace to the chloroplast which needs to be considered (Evans et al., 1986; Evans and Von Caemmerer, 1996). Evans and Von Caemmerer (1991) assumed that the CO_2 transfer conductance from the substomatal cavities to the sites of carboxylation in the chloroplast, g_i, would be constant for a leaf since it is to a large degree related to the anatomy of the leaf such as the chloroplast surface area appressing intercellular airspace. The explicit

inclusion of a constant CO_2 transfer conductance, g_i, from the sub stomatal cavities to the carboxylation sites leads to a quadratic relationship between CO_2 assimilation rate, A and the intercellular CO_2 partial pressure, C_i. The relationship between A and g_i is given by

$$A = g_i (C_i - C_c), \qquad (9.27)$$

and solving for C_c and combining with Eq. (9.9) or Eq. (9.14) one obtains the following two quadratic equations:

$$A_c{}^2 - A_c \left\{ g_i \left(C_i + K_c \left(1 + O/K_o \right) \right) + V_{c\max} + R_d \right\} \\ + g_i \{ V_{c\max} (C_i - \Gamma^*) \\ - R_d \left(C_i + K_c \left(1 + O/K_o \right) \right) \} = 0 \\ (9.28)$$

and

$$A_j{}^2 - A_j \left\{ g_i (C_i + 2\Gamma^*) + J/4 + R_d \right\} \\ + g_i \{ (C_i - \Gamma^*) J/4 \qquad (9.29) \\ - R_d (C_i + 2\Gamma^*) \} = 0.$$

The presence of a significant internal diffusion resistance to CO_2 affects both the quantitative relationship between CO_2 assimilation rate and maximal Rubisco activity and the shape of the CO_2 response curve. The internal conductance to CO_2 has been estimated in various ways: by concurrent measurements of carbon isotope discrimination (Evans et al., 1986; Von Caemmerer and Evans, 1991; Evans and Von Caemmerer, 1996; Hanba et al., 2004; Yamori et al., 2006a), by combined measurements of chlorophyll fluorescence and gas exchange (Evans and Von Caemmerer, 1996; Bernacchi et al., 2002; Flexas et al., 2006, 2007a; Warren and Dreyer, 2006; Warren, 2007) or by fitting Eqs. (9.27) and (9.28) to CO_2 response curves (Ethier and Livingston, 2004; Ethier et al., 2006; Sharkey et al., 2007). There is active research in examining the temperature response of g_i and it appears that g_i increases with temperature but there is species to species variation in this response (Bernacchi et al., 2002; Warren and Dreyer, 2006; Yamori et al., 2006a). A review of temperature dependencies was given by Warren (2008). There has been a recent report that suggests that g_i may vary with both pCO_2 and irradiance, which would make the approach of deriving g_i from a fit of Eqs. (9.28) and (9.29) invalid (Flexas et al., 2007a).

VI. Predicting Photosynthesis from Chloroplast Biochemistry

A. Environmental Responses

The model provides predictions on how the CO_2 assimilation rate varies with pCO_2, pO_2, irradiance and temperature. Many of these predictions were discussed by Farquhar et al. (1980) and one such example is given in Fig. 9.5, which shows the predicted CO_2 assimilation rate at different irradiances and pCO_2. The model predicts that CO_2 assimilation rate is independent of
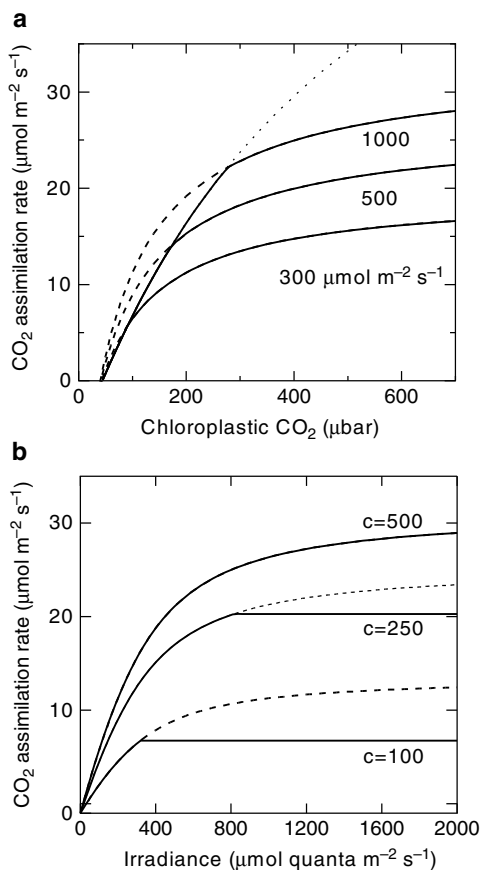
Fig. 9.5. (**a**) Modeled CO_2 assimilation rate (solid lines) as a function of chloroplast pCO_2 at three different irradiances. The extensions of the Rubisco limited rate A_c (dotted line) and the electron transport limited rate A_j (dashed lines) are also shown. Parameters used are given in Table 9.1. Leaf temperature was assumed to be $25\,^{\circ}C$ and $pO_2 = 200\,\mathrm{mbar}$. (**b**) Modeled CO_2 assimilation rate (solid lines) as a function of irradiance at three different chloroplast pCO_2. The electron transport limited rates A_j (dashed lines) are also shown. Other details are as in (**a**)

irradiance (except at very low irradiance) at low pCO_2 where CO_2 assimilation rate is limited by (in this case) fully active Rubisco, whereas at high pCO_2 it is determined by the electron transport limited rate. This suggested that the initial slope of the CO_2 assimilation rate vs. pCO_2 curve can be quantitatively related to V_{cmax} as was done by Von Caemmerer and Farquhar (1981). The modeled irradiance response curves predict that the light saturation of CO_2 assimilation rate depends on pCO_2, a fact which is often ignored. Model predictions can be tested by gas exchange measurements and are useful in planning experiments (Von Caemmerer and Farquhar, 1981). The model also predicted the measured changes in quantum yield with pCO_2 and temperature (Ehleringer and Björkman, 1977), the linear dependence of the CO_2 compensation point on O_2 partial pressure (Laing et al., 1974) and its dependence on respiration rate (Farquhar and Von Caemmerer, 1982). The ability of the model to accurately predict variation of CO_2 assimilation rate with temperature will depend on gaining a better understanding of the modulation of Rubisco activation state with temperature (see Section V.B.)

B. Photosynthesis for Photosynthetic Mutants

Recent advances in chloroplast transformation have made it possible to engineer tobacco expressing mutant Rubiscos (Whitney et al., 1999; Whitney and Andrews, 2003). Using the in vitro kinetic constants of those Rubiscos it was possible to use the model to predict the characteristics of the expected CO_2 assimilation rate of these plants (Fig. 9.6). Whitney et al. (1999) also used the model in the reverse direction and predicted Rubisco kinetic properties from gas exchange measurements. This example highlights the predictive power of the model. An elegant application of the model to the question of how will canopy photosynthesis be affected if we could engineer plants with different Rubiscos was given by Zhu et al. (2004), exemplifying the use of the model to answer a "what if" question.

C. Integration of the Leaf Photosynthesis Model with Stomatal Models

Photosynthesis and transpiration by leaves in nature is determined by the photosynthetic activity of the mesophyll cells within the leaf and by
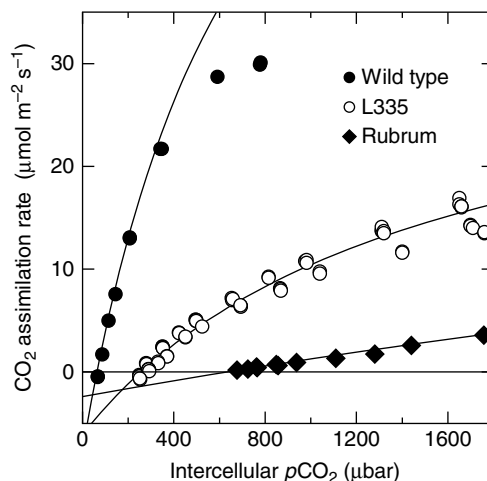

Fig. 9.6. CO_2 assimilation rate, A, as a function of intercellular pCO_2 for a leaf of a wild type (●), transgenic tobacco with a mutant Rubisco where the Leu335 was changed to a Val (○), transgenic tobacco where native Rubisco was replaced by Rubisco from *Rhodospirillum rubrum* (◆). Measurements were made at an irradiance of 1,000 µmol quanta m^{-2} s^{-1} and a leaf temperature of 25 °C at $pO_2 = 200$ mbar. The lines are A predicted from the Rubisco limited rate (Eq. 9.9). For the L335 mutant tobacco $V_{cmax} = 37$ µmol m^{-2} s^{-1}, $K_c = 318$ µbar, $K_o = 55.6$ mbar, $\Gamma^* = 140$ µbar and $R_d = 2.5$ µmol m^{-2} s^{-1}. For the *R. rubrum* tobacco mutant $V_{cmax} = 42$ µmol m^{-2} s^{-1}, $K_c = 4,461$ µbar, $K_o = 126$ mbar, $\Gamma^* = 415$ µbar and $R_d = 1$ µmol m^{-2} s^{-1} (Whitney et al., 1999; Whitney and Andrews, 2001; Mueller-Cajar et al., 2007)

the diffusive conductance of the epidermis that separates the intercellular air space from the surrounding atmosphere. Diffusion may be thought of as the supply function and biochemical processes as the demand function for CO_2 and the pCO_2 within the intercellular air spaces of the leaf is determined by the interaction of supply and demand. Figure 9.7 shows a graphical solution for the intercellular pCO_2 at which the rate of diffusion of CO_2 into the leaf exactly matches the rate of CO_2 uptake by the leaf cells. Given a value for conductance, the ambient pCO_2, and the inputs required for the biochemical model, one can develop an analytical solution or use a computer program to seek the intercellular pCO_2 that satisfies both the supply and demand functions.

The biochemical model has been widely used in this way to examine physiological responses of leaves in natural environments (e.g. Tenhunen et al., 1994). However, a major limitation of this
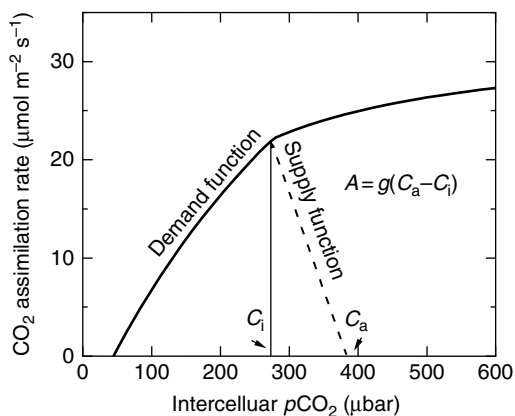
Fig. 9.7. CO$_2$ assimilation rate, *A*, versus intercellular *p*CO$_2$. The solid line indicates the "demand function" the dependence of *A* on intercellular *p*CO$_2$. The dashed line indicates the "supply function", the equation describing the gaseous diffusion of CO$_2$ from the atmosphere to the intercellular spaces. In this diagram the *p*CO$_2$ at the site of carboxylation is assumed to be equal to the *p*CO$_2$ in the intercellular space

approach is that conductance itself is a dynamic and regulated property of the leaf. Variation of conductance can have very profound effects on energy and water exchange by leaves in nature, modifying not only the intercellular *p*CO$_2$, but also the physical environment (principally temperature and water potential) of the mesophyll cells. Therefore, an understanding of the full extent of physiological control of photosynthesis and transpiration of leaves in nature requires a second model capable of predicting stomatal conductance that could be coupled to the photosynthesis model.

Models of stomatal response to environmental variables had long been available (e.g. Jarvis, 1976; see also Collatz et al., 1991), but these considered conductance as separate from photosynthesis and proved difficult to integrate with a photosynthesis model. Systematic measurements of stomatal conductance and photosynthesis to changes in light, *p*CO$_2$, leaf temperature and atmospheric humidity were used by Ball et al. (1987) to develop an empirical relationship for stomatal conductance as a function of CO$_2$ assimilation rate:

$$g = m \cdot A \cdot h_s / C_s + b, \qquad (9.30)$$

where *m* and *b* are regression coefficients, *A* is the rate of net CO$_2$ assimilation, and h_s and C_s

are the partial pressure of water vapor and CO$_2$ at the surface of the leaf – inside the laminar boundary layer. It is of interest that without some independent means of predicting the rate of photosynthesis, the Ball et al. model would have no predictive value. On the other-hand, when used together with a photosynthesis model the terms for the response to temperature, light intensity and leaf to leaf variation in humidity deficit and water potential used in other models of stomatal conductance (e.g. Jarvis, 1976) are subsumed in the response of *A* to these variables, making it easier to combine these models. This linkage of stomatal conductance to *A* was indicated by Wong et al. (1979, 1985), who showed that stomatal conductance of leaves during steady-state photosynthesis is strongly correlated with the rate of CO$_2$ assimilation, and it is consistent with the theoretical arguments on optimal control of stomatal conductance proposed by Cowan and Farquahr (1977).

Ball (1988), Tenhunen et al. (1990), Leuning (1990), Collatz et al. (1991, 1992) and Harley et al. (1992) developed coupled models of photosynthesis, transpiration and the leaf energy budget using the Ball et al. (1987) stomatal model and the Farquhar et al. (1980) photosynthesis model. Lloyd and Farquhar (1994) and Leuning et al. (1995) have developed alternative stomatal models for use in coupled model systems. These coupled models are now widely used to simulate carbon, water and energy exchange at the scale of fields (de Pury and Farquhar, 1997) ecosystems (Colello et al., 1998) and the globe (Randall et al., 1996).

Baldocchi (1994) proposed an analytical solution to a coupled system of models arguing that iterative solutions were unreliable. One factor contributing to this problem is that the approach of taking the minimum of the rates of the potential biochemical processes leads to discontinuities or "breaks" in the response curve at the transitions from one factor to the next (Fig. 9.1). Collatz et al. (1991) addressed this problem by using quadratic equations of the form

$$\theta J^2 - J(J_1 + J_2) + J_1 J_2 = 0, \qquad (9.31)$$

where the value of *J* obtained from the root is the minimum of J_1 and J_2 with a smooth transition between these with a curvature in the transition

defined by the parameter, $\theta(1 < \theta > 0)$. Two quadratic equations can be used in sequence to select among three potential limitations. The C$_3$ and C$_4$ models presented by Collatz et al. (1991, 1992) are structured such that expressions for the potential limiting processes unique to each pathway are processed by identical quadratic expressions making it possible to easily switch between pathways in the same subroutine. This approach yields very similar answers to the original Farquhar et al. implementation with continuous functions of net CO$_2$ assimilation leading to robust iterative solutions.

D. Canopy Photosynthesis

Leaf models are now commonly used as a basis for simulating the water, carbon and energy exchange of plant canopies consisting of millions of leaves. Calibration of these models is largely based on leaf scale measurements with only limited constraint from measurements such as eddy correlation at the scale of application. The accuracy of such models is therefore highly dependent on the assumptions used in integrating from the leaf to the canopy scale. Heterogeneity in the thermal, aerodynamic and light climates within the canopy is important as is the corresponding heterogeneity in the property of leaves that develop in different positions within the canopy. This is a complex area that is beyond the scope of this review. The reader is referred to papers by de Pury and Farquhar (1999), Wang and Leuning (1999), Baldocchi et al. (2002) and to Chapter 16 by Ülo Niinemets and Niels P. R. Anten and Chapter 18 by Manfred Küppers and Michael Pfiz. Interestingly, this has become an important approach for simulating the conductance of vegetated land surfaces to water vapor. This is a critical parameter controlling the partitioning of absorbed radiation to sensible heat or evaporation of water – an important driver of the physical climate system. The reader is referred to Sellers et al. (1997) for a review of this topic.

VII. Predicting Chloroplast Biochemistry from Leaf Gas Exchange

The C$_3$ model is most often used to infer chloroplast biochemistry from gas exchange measurements (Ainsworth et al., 2002; Leuning, 2002;

Medlyn et al., 2002; Long and Bernacchi, 2003; Ethier and Livingston, 2004; Sharkey et al., 2007). Von Caemmerer and Farquhar (1981, 1984) compared in vitro measurements of Rubisco activity and chloroplast electron transport with gas exchange measurements and showed that they could be quantitatively related to gas exchange measurements made in *Phaseolus vulgaris* grown under different environmental conditions. It is often easier to infer leaf biochemistry from gas exchange measurements than make the required in vitro measurements especially since it is difficult to extract functional enzymes from many species. Long and Bernacchi (2003) provide an excellent review and discussion of how to best make these measurements. A routine that facilitates the fitting of gas exchange data has been provided by Sharkey et al. (2007).

It is possible to determine whether RuBP regeneration capacity (including electron transport capacity) limits CO$_2$ assimilation rate from measurements of CO$_2$ responses and calculations of the RuBP regeneration rate, as well as other fluxes, such as of FBP formation and consumption and electron transport rate required to support measured CO$_2$ assimilation rates (Farquhar and Von Caemmerer, 1982; Brooks and Farquhar, 1985; Von Caemmerer and Quick, 2000). An example is solving for the actual electron transport rate J_a using Eq. (9.14) as was done by Von Caemmerer and Farquhar (1981). It can be seen (Fig. 9.8) that J_a calculated form A increases with increasing intercellular pCO_2 and then becomes constant at higher C_i. A constant J_a can be taken as an indication of an electron transport limitation (although some caution is needed, especially at high irradiance, as other components of RuBP regeneration have the same relative dependencies on pCO_2 and pO_2). Triose phosphate limitation may also occur at high pCO_2, but should cause J_a to decrease with increasing pCO_2. Note that CO$_2$ assimilation rate continues to increase with increasing C_i as energy consumption is diverted from photorespiration to carboxylation. The calculated electron transport rate was confirmed with concomitant measurements of the quantum yield of PS II (ϕ_{PSII}) from chlorophyll fluorescence, which is proportional to chloroplast electron transport rate at a given irradiance (Genty et al., 1989).

Combined measurements of gas exchange and chlorophyll fluorescence have become a popular
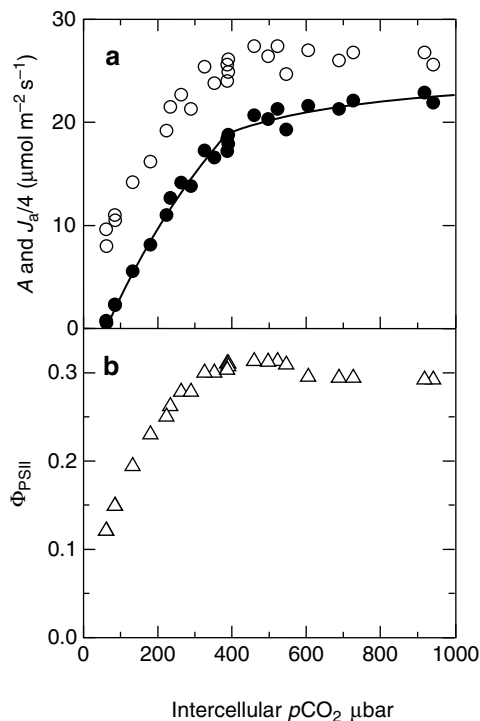
Fig. 9.8. (**a**) CO_2 assimilation rate, *A*, and calculated actual chloroplast electron transport rate, $J_a/4$, as functions of intercellular pCO_2 for a tobacco leaf. Measurements were made at an irradiance of 1,000 μmol quanta $m^{-2}\,s^{-1}$, leaf temperature of 25 °C and $pO_2 = 200$ mbar. $J_a/4$ was calculated from CO_2 assimilation rate by estimating chloroplast pCO_2 from Eq. (9.26) with an internal conductance $g_i = 0.3$ mol $m^{-2}\,s^{-1}\,bar^{-1}$ (data from Hudson et al., 1992). (**b**) The quantum yield of PS II (Φ_{PSII}) estimated from chlorophyll fluorescence measured concurrently with gas exchange. Chlorophyll fluorescence was measured on the adaxial surface and Φ_{PSII} was calculated according to Genty et al. (1989)

tool to assess chloroplast biochemistry (Long and Bernacchi, 2003). The chlorophyll fluorescence provides an excellent way to distinguish RuBP regeneration limited CO_2 assimilation rate from Rubisco limited rate, because chloroplast electron transport calculated from fluorescence becomes independent of pCO_2 when RuBP regeneration limits CO_2 assimilation rate (Fig. 9.8). We believe that this is a useful tool at low light or temperature extremes where it may be difficult to distinguish an RuBP regeneration limitation from a Rubisco limitation. The

quantitative comparison between CO_2 assimilation rate measurements and chlorophyll fluorescence measurements can however be more problematic as the two measurements average different chloroplast populations of the leaf.

If estimates of V_{cmax} and *J* are to be related to other leaf measurements such as nitrogen or chlorophyll content, it is important to also estimate the conductance to internal CO_2 diffusion as otherwise these parameters will be underestimated (Long and Bernacchi, 2003; Ethier and Livingston, 2004; Ethier et al., 2006; Warren, 2007). Careful measurements of CO_2 and light response curves over a range of temperature have been valuable in providing in vivo temperature responses for both Rubisco and electron transport parameters and provide a means for species comparisons (Kirschbaum and Farquhar, 1984; Von Caemmerer et al., 1994; Walcroft et al., 1997; Bernacchi et al., 2001, 2002, 2003).

VIII. Concluding Remarks

The photosynthesis model described here provides a quantitative framework that can be used as a research tool to design and interpret both field and laboratory based experiments. The papers cited here represent only a small fraction of studies that have used the model to interpret results. Both in vivo and in vitro studies have provided us with parameterization of the Rubisco limited CO_2 assimilation rate and studies with transgenic plants with mutant Rubiscos have highlighted the predictive power of the model in this regard. An elegant application of the model to the question of how will canopy photosynthesis be affected if we could engineer plants with different Rubiscos was given by Zhu et al. (2004), exemplifying the use of the model to answer "what if" questions. However there are three main areas were further research is needed. We need to learn more about what governs Rubisco activation in vivo, work towards a more mechanistic understand of what determines chloroplast electron transport rate and the conductance to CO_2 diffusion from intercellular airspace to the chloroplast.

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