

# Mathematical Analysis of Cell CO<sub>2</sub> Exchange Under High CO<sub>2</sub> Concentrations\*

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## Abstract

An approximate solution describing net CO<sub>2</sub> exchange by spherical cells subjected to high CO<sub>2</sub> concentrations (greater than 1000 cm<sup>3</sup> m<sup>-3</sup>) was derived from a second-order, ordinary differential equation. We assumed that the sinks and sources of CO<sub>2</sub> were uniformly distributed in the protoplasm and could be expressed by Michaelis-Menten equations. The photosynthetic rate of the cell was mathematically derived to be dependent in a fairly complex relationship on the biochemistry of carboxylation and photorespiration, dark respiration, and the geometry of the cell. These characteristics of the photosynthesizing cell were also found to affect the derived expression for quantum efficiency.

The physical and biochemical interpretation of CO<sub>2</sub> exchange by leaves in response to light, CO<sub>2</sub>, and oxygen has been fairly ambiguous. While models of leaf CO<sub>2</sub> assimilation have been published, they invariably contain empirical parameters which are equivocal. For example, the models of HALL (1971) and CHARTIER and PRIOUL (1976) are each based on contrived equations for photosynthesis which are driven by unknown reaction rates. These reaction rates are only determined by comparing leaf gas exchange rates with their system of equations. Unfortunately, they tend to provide little fundamental insight about the direct effects of biochemistry and morphology on photosynthesis.

On the other hand, SINCLAIR *et al.* (1977) recently derived an expression for net CO<sub>2</sub> assimilation by photosynthesizing cells involving a second-order, ordinary differential equation for diffusion in a sphere containing uniformly distributed sinks and sources of CO<sub>2</sub>. Their derivation ultimately collapsed into the familiar form of the leaf photosynthetic equation, including terms for a mesophyll resistance and CO<sub>2</sub> compensation point. The mesophyll resistance and CO<sub>2</sub> compensation point were unambiguously defined in their derivations by the photosynthetic biochemistry and by the cell and leaf geometry. Nevertheless, the derivation of SINCLAIR *et al.* (1977) was achieved only by assuming that in the intercellular air-space, CO<sub>2</sub> concentrations were significantly less than the Michaelis-Menten constant for CO<sub>2</sub> of carboxylation. These restricting conditions are generally met only when the ambient CO<sub>2</sub> concentrations are maintained at below normal atmospheric concentrations, or when the photosynthetic rate is high and the stomatal resistance is sufficiently large to result in these reduced CO<sub>2</sub> concentrations in the intercellular airspaces.

In this paper, we extend this basic, theoretical analysis of CO<sub>2</sub> diffusion into photosynthesizing cells by considering the situation where the intercellular CO<sub>2</sub> concentration is high. We will also assume a spherical cell and use the Michaelis-Menten expression for CO<sub>2</sub> and O<sub>2</sub> competition at the carboxylating enzyme. Finally, we present a derivation defining the quantum yield of whole cells under high CO<sub>2</sub> concentration.

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## 240 THE MODEL

Assuming radial symmetry, the steady state diffusion of  $\text{CO}_2$  in a spherical cell is governed by the following second-order, ordinary differential equation:

$$\frac{D}{r^2} \frac{d}{dr} \left( r^2 \frac{dC}{dr} \right) = \Phi, \quad (1)$$

where  $C = C(r) = \text{CO}_2$  concentration at position  $r$  [ $\text{g cm}^{-3}$ ],  $r =$  distance from center of cell [cm],  $D =$  diffusion coefficient [ $\text{cm}^2 \text{s}^{-1}$ ],  $\Phi =$  net  $\text{CO}_2$  uptake [ $\text{g cm}^{-3} \text{s}^{-1}$ ].

The sinks of  $\text{CO}_2$  (carboxylation) and sources of  $\text{CO}_2$  (photorespiration and dark respiration) are assumed to be uniformly distributed throughout the protoplasm. While this assumption is a simplified approximation to the situation inside a real cell, we feel it is a much more accurate representation of a cell than the plane of sinks and sources which is generally assumed. The net  $\text{CO}_2$  uptake  $\Phi$  may be written

$$\Phi = \Phi_{\text{chl}} - \Phi_{\text{pr}} - \Phi_{\text{dr}}, \quad (2)$$

where  $\Phi_{\text{chl}} =$  chloroplastic carboxylation,  $\Phi_{\text{pr}} =$  photorespiration,  $\Phi_{\text{dr}} =$  dark respiration. Dark respiration, for this analysis, is assumed independent of the  $\text{CO}_2$  and  $\text{O}_2$  concentration gradients occurring within the cell and is held constant.

Michaelis-Menten expressions are used to define the dependence of  $\Phi_{\text{chl}}$  and  $\Phi_{\text{pr}}$  on  $\text{CO}_2$  and  $\text{O}_2$  concentrations. LAING *et al.* (1974) found that  $\text{CO}_2$  assimilation and photorespiration in  $\text{C}_3$  plants is a result of competitive inhibition of  $\text{CO}_2$  and  $\text{O}_2$  on the RuDP carboxylase. The complete Michaelis-Menten expressions for these reactions, given by LAING *et al.*, are as follows:

$$\Phi_{\text{chl}} = \frac{V_c K_o C}{K_c K_o + K_o C + K_c O} \quad (3)$$

$$\Phi_{\text{pr}} = \frac{t V_o K_c O}{K_c K_o + K_o C + K_c O} \quad (4)$$

where  $V_c =$  maximum enzymatic velocity for carboxylase reaction [ $\text{g cm}^{-3} \text{s}^{-1}$ ],  $V_o =$  maximum enzymatic velocity for oxygenase reaction [ $\text{g cm}^{-3} \text{s}^{-1}$ ],  $K_c =$  Michaelis-Menten constant for  $\text{CO}_2$  [ $\text{g cm}^{-3}$ ],  $K_o =$  Michaelis-Menten constant for  $\text{O}_2$  [ $\text{g cm}^{-3}$ ],  $O =$   $\text{O}_2$  concentration [ $\text{g cm}^{-3}$ ],  $t =$  fraction of  $\text{CO}_2$  evolved in photorespiratory pathway per  $\text{O}_2$  consumed.

We desire a solution  $C = C(r)$  to Eqs. (1) to (4) which satisfies an assumed boundary condition of no net  $\text{CO}_2$  flux into the vacuole. That is,

$$\frac{dC}{dr} = 0 \quad \text{when} \quad r = R_{\text{vac}} \quad (5)$$

where  $R_{\text{vac}} =$  tonoplast radius [cm].

In addition to depending upon the parameters already listed above, the solution  $C(r)$  will also depend on  $C_o$ , the concentration of  $\text{CO}_2$  at the plasmalemma,

$$C = C_o \quad \text{when} \quad r = R \quad (6)$$

where  $R =$  plasmalemma radius [cm].

A closed form solution to Eqs. (1) to (6) is unavailable. SINCLAIR *et al.* (1977) obtained an approximate solution valid when  $C_o \ll K_c$ , that is under saturating irradiance or low  $\text{CO}_2$  concentrations. In this paper, we present an approximate solution valid when  $C_o \gg K_c$ . We expect this

solution to be relevant to the cases where irradiances are low and the CO<sub>2</sub> concentrations are elevated.

The following approximate solution to Eqs. (1) to (6), valid for  $C_o \gg K_c$ , is derived in the Appendix:

$$C(r) = C_o + \frac{V_c R^2}{6D} \left[ 1 - \frac{\Phi_{dr}}{V_c} - \frac{K_c}{C_o} \left( 1 + \frac{O}{K_o} + \frac{tV_o O}{V_c K_o} \right) \right] \cdot \left[ \frac{r^2}{R^2} - 1 + 2 \left( \frac{R_{vac}}{R} \right)^3 \left( \frac{R}{r} - 1 \right) \right] \quad (7)$$

Comparison of this equation with a finite difference numerical integration of Eqs. (1) to (6) showed that  $C_o/K_c$  must be larger than about 3 for reasonable accuracy. Since BAHR and JENSEN (1974) found the value of  $K_c$  for ribulose diphosphate carboxylase extracted from tobacco and spinach to be approximately equivalent to  $350 \text{ cm}^3 \text{ m}^{-3}$ , this means that we assume the intercellular CO<sub>2</sub> concentration is at least  $1000 \text{ cm}^3 \text{ m}^{-3}$ .

The photosynthetic rate  $P_n$  equals the net CO<sub>2</sub> flux into the cell (taken per unit cell surface area):

$$P_n = D \frac{dC}{dr} \Big|_{r=R} = \frac{V_c R}{3} \left[ 1 - \frac{\Phi_{dr}}{V_c} - \frac{K_c}{C_o} \left( 1 + \frac{O}{K_o} + \frac{tV_o O}{V_c K_o} \right) \right] \left[ 1 - \left( \frac{R_{vac}}{R} \right)^3 \right] \quad (8)$$

Finally, Eq. (8) is differentiated with respect to  $V_c$  to obtain an expression used later. We will assume for this differentiation that  $V_o$  is approximately some constant fraction,  $\xi$ , of  $V_c$ . Therefore,

$$\frac{dP_n}{dV_c} = \frac{R}{3} \left[ 1 - \frac{K_c}{C_o} \left( 1 + \frac{O}{K_o} + t\xi \frac{O}{K_o} \right) \right] \left[ 1 - \left( \frac{R_{vac}}{R} \right)^3 \right] \quad (9)$$

## DISCUSSION

No simple analytical expression, which defines a cellular resistance to CO<sub>2</sub> flow or a compensation point, is apparent in Eq. (8). The photosynthetic rate is, in fact, found to be dependent on the cell geometry ( $R$ ,  $R_{vac}$ ) and biochemistry ( $V_c$ ,  $V_o$ ,  $K_c$ ,  $K_o$ ,  $\Phi_{dr}$ ).

The derived expression (8) for photosynthetic rate under high CO<sub>2</sub> concentrations suggests a strong dependence on maximum carboxylation velocity,  $V_c$ . Unlike the derivation of SINCLAIR *et al.* (1977) under low CO<sub>2</sub> concentrations, where  $P_n$  is proportional to  $\sqrt{V_c}$ , Eq. (8) indicates a nearly linear relationship. The dependence of this derived photosynthetic rate on cellular biochemical activity agrees with the observation of GAASTRA (1959) of high temperature sensitivity in net CO<sub>2</sub> exchange rates under high CO<sub>2</sub> concentrations.

Initially surprising is the nearly linear relationship of  $P_n$  on cell radius. However, Eq. (8) defines the flux density per unit surface area so to estimate the total flux into a cell the effect of changing surface area with radius must be considered. Consequently, the total flux into the cell changes with the third power of the radius as does the volumetric content of the cell.

There is less dependence of the derived photosynthetic rate on the other biochemical variables. Increasing dark respiration rates clearly reduces the net CO<sub>2</sub> exchange. However, it is the ratio of  $\Phi_{dr}/V_c$  which is critical, and a sufficiently large value of  $V_c$  will result in a minimal effect

242 from  $\Phi_{dr}$ . The variables which characterize oxygenase activity are grouped together in one term. Stimulation of photorespiration through increased  $O_2$  concentration or  $V_o$ , or decreased  $K_o$  will result in decreased net  $CO_2$  exchange. However, this photorespiratory term is multiplied by the ratio  $K_c/C_o$  which was already assumed to be much less than one. Therefore, it is expected that the effect of photorespiration on photosynthetic activity under high  $CO_2$  concentrations will be minimal. These conclusions based on the mathematical analysis agree closely with the data of Fock *et al.* (1971) on sunflower and *Chlorella*. At 2%  $O_2$ , increasing  $CO_2$  above  $1000\text{ cm}^3\text{ m}^{-3}$  had no effect on the observed exchange rate of  $CO_2$ . When the  $O_2$  concentration was 44% there were small increases in  $CO_2$  uptake rates as the  $CO_2$  concentration was increased from  $1000$  to  $5000\text{ cm}^3\text{ m}^{-3}$ .

Eq. (8) indicates that the effect of the vacuole size on  $CO_2$  exchange under high  $CO_2$  concentrations is minimal. This is because  $R_{vac}$  is less than the cell radius  $R$ , and the ratio of these radii is taken to the third power. Only when the vacuole radius is a large fraction of the cell radius is there expected to be a marked decrease in photosynthetic rates.

The differentiation of  $P_n$  with respect to  $V_c$  leads to an approximate expression for the photosynthetic quantum yield. That is, we assume the maximum carboxylation rates under high  $CO_2$  concentrations are mostly determined by the availability of reductant. Assuming the reductant availability is nearly linearly proportional to the quantum input into the photochemistry, Eq. (9) approximates the change in  $CO_2$  assimilation with respect to a change in light. The proportionality constant,  $\alpha$ , between  $CO_2$  fixed and quanta required is generally assumed to be maximally  $1\text{ }\mu\text{mol } CO_2$  fixed per  $8\text{ }\mu\text{einstein}$  (CLAYTON 1971). Finally, to put Eq. (9) in a dimensionless form, the difference in units between  $P_n$ , expressed per unit cell surface, and  $V_c$ , expressed on a volumetric basis, must be considered. Consequently, Eq. (9) must be multiplied by the ratio of sphere surface area to volume ( $4\pi R^2/\frac{4}{3}\pi R^3$ ). Then an approximate expression for quantum yield under high  $CO_2$  concentrations becomes

$$\alpha \left[ 1 - \frac{K_c}{C_o} \left( 1 + \frac{O}{K_o} + t\xi \frac{O}{K_o} \right) \right] \left[ 1 - \left( \frac{R_{vac}}{R} \right)^3 \right] \quad (10)$$

Significantly, this derived expression suggests that the quantum yield in intact cells may, in fact, easily be less than  $\alpha$ . The quantum yield for the cell is found to be dependent on  $CO_2$  and  $O_2$  concentrations as well as on the Michaelis-Menten constants for carboxylase and oxygenase. The observed quantum yield approaches  $\alpha$  only when  $CO_2$  concentration is high and  $O_2$  concentration is low. These derived effects of  $O_2$  and  $CO_2$  concentrations agree qualitatively with the experimental data on *Encelia californica*, presented by EHLERINGER and BJÖRKMAN (1977), especially when  $CO_2$  concentration was greater than  $600\text{ cm}^3\text{ m}^{-3}$ . They found under 2%  $O_2$  the quantum yield of the  $C_3$  species was unaffected by  $CO_2$  concentration. In 21%  $O_2$ , increasing  $CO_2$  concentration increased the quantum yield but the values were still less than those for 2%  $O_2$ .

Another interesting conclusion from Eq. (10) is that the quantum yield of intact cells is dependent on cell geometry by the ratio of the vacuole radius to cell radius. Since this ratio is raised to the third power, the vacuole radius must be substantial before the quantum yield is markedly reduced. Nevertheless, this derived expression suggests that the maximal quantum yield is achieved only when no vacuole exists.

## CONCLUSION

By restricting the analysis of the second order ordinary differential equation for  $CO_2$  diffusion in a sphere to high  $CO_2$  concentration (greater than  $1000\text{ cm}^3\text{ m}^{-3}$ ), a solution for the  $CO_2$  concentrations in the sphere and net  $CO_2$  flux density per unit surface area is obtained. This

solution of CO<sub>2</sub> assimilation cannot be condensed to a simple resistance equation, as found by SINCLAIR *et al.* for the case of low CO<sub>2</sub> concentrations. Instead the CO<sub>2</sub> flux density, for a cell is nearly linearly dependent on the maximum carboxylation velocity ( $V_c$ ) and cell radius. The derived expression explicitly defines the reduction in photosynthetic rates due to dark respiration and photorespiration. The size of the vacuole can also result in reduced photosynthetic activity when its radius is large relative to the cell radius.

The quantum efficiency for whole cells under high CO<sub>2</sub> concentrations is similarly found to be dependent on the biochemistry of carboxylation and photorespiration as well as cell geometry. The concentrations of O<sub>2</sub> and CO<sub>2</sub> were derived to be variables directly affecting the quantum yield observed for the whole cell. The quantum yield of intact cells can apparently only attain the maximal value,  $\alpha$ , under rather unique conditions.

## APPENDIX

In terms of the dimensionless variables

$$x = r/R \quad (\text{A1})$$

$$y = C/K_c \quad (\text{A2})$$

Eqs. (1) to (6) become

$$\frac{1}{x^2} \frac{d}{dx} \left( x^2 \frac{dy}{dx} \right) = \frac{Ay - B}{y + G} \quad (\text{A3})$$

$$\frac{dy}{dx} = 0, \quad x = \lambda \quad (\text{A4})$$

$$y = \varepsilon, \quad x = 1 \quad (\text{A5})$$

where

$$A = \frac{V_c R^2}{K_c D} \left( 1 - \frac{\Phi_{dr}}{V_c} \right)$$

$$B = \frac{V_c R^2}{K_c D} \left[ t \frac{V_o}{V_c} \frac{O}{K_o} + \frac{\Phi_{dr}}{V_c} \left( 1 + \frac{O}{K_o} \right) \right]$$

$$G = 1 + \frac{O}{K_o}$$

$$\lambda = R_{vac}/R$$

$$\varepsilon = C_o/K_c$$

We obtain a solution  $y(x)$  valid for  $\varepsilon \gg 1$  in the form of a power series in  $1/\varepsilon$ :

$$y(x) = \varepsilon y_0(x) + y_1(x) + 1/\varepsilon y_2(x) + \dots \quad (\text{A6})$$

244 Note that Eq. (A3) is nonlinear and hence difficult to solve. Substituting Eq. (A6) into Eqs. (A3) to (A5), collecting terms, and equating to zero the coefficients of  $\epsilon$ , 1, and  $1/\epsilon$ , respectively, gives linear equations and boundary conditions on  $y_0(x)$ ,  $y_1(x)$  and  $y_2(x)$ . Solving these equations, we obtained:

$$y_0(x) = 1$$

$$y_1(x) = \frac{A}{6} x^2 + \frac{A \lambda^2}{3x} - \frac{A}{6} (1 + 2 \lambda^3)$$

$$y_2(x) = -\frac{(B + AG)}{6} \left[ x^2 + \frac{2 \lambda^3}{x} - (1 + 2 \lambda^3) \right]$$

Substituting these expressions into Eqs. (A6) and (A2) gives Eq. (7) of the text.

## REFERENCES

- BAHR, J. T., JENSEN, R. G.: Ribulose diphosphate carboxylase from freshly ruptured spinach chloroplasts having an *in vivo*  $K_m$  [CO<sub>2</sub>]. — *Plant Physiol.* **53**: 39–44, 1974.
- CHARTIER, P., PRIOUL, J. L.: The effects of irradiance, carbon dioxide and oxygen on the net photosynthetic rate of the leaf: A mechanistic model. — *Photosynthetica* **10**: 20–24, 1976.
- CLAYTON, R. K.: *Light and Living Matter*. Vol. 2: The Biological Part. — McGraw-Hill Inc., New York 1971.
- EHLERINGER, J., BJÖRKMAN, O.: Quantum yields for CO<sub>2</sub> uptake in C<sub>3</sub> and C<sub>4</sub> plants. Dependence on temperature, CO<sub>2</sub>, and O<sub>2</sub> concentration. — *Plant Physiol.* **59**: 86–90, 1977.
- FOCK, H., CANVIN, D. T., GRANT, B. R.: Effects of oxygen and carbon dioxide on photosynthetic O<sub>2</sub> evolution and CO<sub>2</sub> uptake in sunflower and *Chlorella*. — *Photosynthetica* **5**: 389–394, 1971.
- GAASTRA, P.: Photosynthesis of crop plants as influenced by light, carbon dioxide, temperature, and stomatal diffusion resistances. — *Med. Landbouwhogeschool Wageningen* **59** (13): 1–68, 1959.
- HALL, A. E.: A model of leaf photosynthesis and respiration. — *Carnegie Inst. Year Book* **70**: 530–540, 1971.
- LAING, W. A., OGREN, W. L., HAGEMAN, R. H.: Regulation of soybean net photosynthetic CO<sub>2</sub> fixation by the interaction of CO<sub>2</sub>, O<sub>2</sub>, and ribulose 1,5-diphosphate carboxylase. — *Plant Physiol.* **54**: 678–685, 1974.
- SINCLAIR, T. R., GOUDRIAAN, J., DE WIT, C. T.: Mesophyll resistance and CO<sub>2</sub> compensation concentration in leaf photosynthesis models. — *Photosynthetica* **11**: 56–65, 1977.