An elucidatory model of oxygen's partial pressure inside substomatal cavities

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Abstract. A parsimonious model based on Dalton's law reveals substomatal cavities to be dilute in oxygen (O_2), despite photosynthetic O_2 production. Transpiration elevates the partial pressure of water vapour but counteractively depresses those of dry air's components – proportionally including O_2 – preserving cavity pressurization that is negligible as regards air composition. Suppression of O_2 by humidification overwhelms photosynthetic enrichment, reducing the O_2 molar fraction inside cool/warm leaves by hundreds/thousands of ppm. This elucidates the mechanisms that realize O_2 transport: diffusion cannot account for up-gradient conveyance of O_2 from dilute cavities, through stomata to the more aerobic atmosphere. Rather, leaf O_2 emissions depend on non-diffusive transport via mass flow in the form of "stomatal jets" forced by cavity pressurization, which is not negligible in the context of driving viscous flow. Jet expulsion overcomes massive inward O_2 diffusion to force net O_2 emission. At very high leaf temperatures, jets also influence transport of water vapour and carbon dioxide, physically decoupling their exchanges and reducing water-use efficiency, independent of stomatal regulation.

1 Introduction

Plant physiological frameworks appear to have incorrectly described the partial pressures of gases within sub-stomatal cavities, where leaf photosynthesis takes place. That of water vapour (e) is well known to be greatly elevated by transpiration, as reflected by the ambient vapour pressure deficit (VPD). However, both the total pressure (p) and partial pressures of dry air components such as oxygen (p_{O_2}) have been fixed as parameters independent of plant functioning (e.g., Farquhar and Wong,1984), neglecting the consequences of Dalton's law of partial pressures. Here, a very simple model is presented that estimates p_{O_2} with accuracy that is sufficient to elucidate the mechanisms relevant to stomatal gas transport, which are not exclusively diffusive as has long been supposed (Moss and Rawlins, 1963).

2 Physical Law and Theory

Dalton's law of partial pressures,

$$p = e + (p_{N_2} + p_{O_2} + p_{Ar}), \tag{1}$$

defines p as the sum of e with the partial pressure of dry air, within the parentheses, which in turn is the sum of the partial pressures of nitrogen (N_2), O_2 and argon (Ar), neglecting gases with mere trace contributions. Equation (1) can be expressed for both the substomatal cavity interior (i),

$$p_i = e_i + \left(p_{i,N_2} + p_{i,O_2} + p_{i,Ar}\right), \tag{2}$$

as well as for the ambient atmosphere (a) outside the leaf,

$$p_a = e_a + \left(p_{a,N_2} + p_{a,O_2} + p_{a,Ar}\right). \tag{3}$$

If Δ denotes a cavity surplus versus ambient, subtracting Eq. (3) from Eq. (2) yields

$$\Delta p = \Delta e + \left(\Delta p_{N_2} + \Delta p_{O_2} + \Delta p_{Ar}\right), \tag{4}$$

where Δe quantifies cavity humidification and reflects the ambient VPD. In the context of Eq. (4) for substomatal cavities, water vapour's substantial surplus ($\Delta e > 0$) implies either cavity pressurization ($\Delta p > 0$), or depressed partial pressures of dry air's components ($\Delta p_{N_2} + \Delta p_{O_2} + \Delta p_{Ar} < 0$), or a combination of both. Since cavity pressurization would drive mass flow out of the aperture, theoretical considerations from micro-scale fluid dynamics can establish an upper limit for Δp.

Despite the fact that stomata are not cylindrical, the Poiseuille equation derivation (Giancoli, 1984) can be used to show that Δp negligibly counterbalances Δe in Eq. (4). This is done below by exaggerating the parameters of cylindrical geometry to put a bound on the Δp required to force viscous flow. The axial velocity v of a laminar flow through a cylinder of length L and radius R is given as

$$v = \frac{\Delta p}{4\eta L} R^2, \tag{5}$$

where η is air's dynamic viscosity (18 µPa s). Solving for Δp yields

$$\Delta p = \frac{4\eta L v}{R^2}. \tag{6}$$

Here, parameters are chosen so as to maximize the Δp required to drive viscous flow:

- Stomatal dimensions are exaggerated based on Lawson et al. (1998):
    - Pore depth is overestimated as L = 10µm,
    - Stomatal aperture is underestimated using R = 2 µm (area ~ 13 µm^2);

- An air velocity of v = 6 mm s^{-1} escaping the stomatal aperture (Kowalski, 2017) represents an upper bound in the sense that plant physiologists have assumed all transport to be diffusive, with no relevant role played by mass flow, effectively assuming a null value of v.

Plugging these values into Eq. (6) results in Δp = 0.0011 kPa, indicating that a very slight pressure difference is required to drive viscous flow. Given this, in the context of Eq. (4) regarding air composition and with resolution sufficient to characterize the VPD (to +/- 0.01 kPa), we can neglect substomatal pressurization in Eq. (4), taking Δp = 0. This means that any increase in the cavity's Δe forced by transpiration must be counterbalanced by a reduction in the partial pressure of dry air ($\Delta p_{N_2} + \Delta p_{O_2} + \Delta p_{Ar} < 0$).

3 The Model

With transpired water vapour supplanting substomatal dry air, the simplest model is proportional depression of the partial pressures of dry air's components. In light of the Ideal Gas Law this implies that, for every 1000 dry air molecules displaced by water vapour, we can expect N_2 : O_2 : Ar proportions of 781 : 210 : 9. Therefore O_2's partial pressure inside substomatal cavities is modelled succinctly by

$$-\Delta p_{O_2} = 0.210 \cdot \Delta e, \tag{7}$$

indicating O_2 depression (versus ambient) that is 21% of the vapour pressure surplus of the substomatal cavity, or about 21% of the environmental VPD.

4 Model Implications, Uncertainties, and Relevance to Other Gases

Oxygen deficits prevail within substomatal cavities because photosynthetic enrichment (µmol m^{-2} s^{-1}) of O_2 is vastly overwhelmed by O_2 dilution and displacement due to transpiration (mmol m^{-2} s^{-1}). The degree of O_2 depression depends strongly on the VPD, and therefore leaf temperature (T), as illustrated by representative examples of cool and warm leaves (Table 1). Notably, even the cool leaf has a significant O_2 pressure deficit of $-\Delta p_{O_2}$ = 0.066 kPa. "Near sea level" (defined hereinafter as p = 100 kPa), this corresponds to an O_2 molar fraction (referencing moist air) that is 660 ppm below ambient. In warm leaves O_2 depression reaches several thousand ppm, and in torrid environments it can be far greater.

	Cool	**Warm**
T_{leaf}	10ºC	34 ºC
T_{air}	8ºC	30 ºC
e_{leaf}	1.228 kPa	5.325 kPa
e_{air}	0.912 kPa	3.610 kPa
Δe	0.316 kPa	1.715 kPa
$-\Delta p_{O_2}$	0.066 kPa	0.359 kPa
$-\Delta \chi_{O_2}$	660 ppm	3590 ppm

Table 1: Consequences of negligible stomatal-cavity pressurization regarding air composition. Representative temperatures, water vapour pressures, stomatal cavity vapour pressure surplus (Δe), oxygen pressure deficits ($-\Delta p_{O_2}$), and oxygen concentration deficits ($-\Delta \chi_{O_2}$) for cool and warm leaves and their ambient atmospheres. Leaves are taken as saturated and ambient air at 85% relative humidity; $-\Delta p_{O_2}$ is calculated using Eq. (7); $-\Delta \chi_{O_2}$ is calculated for conditions "near sea level" (p = 100 kPa).

The most noteworthy inference from this Daltonian model regards the mechanisms of gas transport through stomata, since O_2 produced by photosynthesis cannot diffuse out of stomata as has been traditionally assumed (Parkhurst, 1994). Equation (7) implies that substomatal cavities are generally much more dilute in O_2 than their environments, whatever the leaf T. Although current thinking in plant physiology would explain O_2 transport in terms of diffusive flows within a ternary system (Jarman, 1974; von Caemmerer and Farquhar, 1981), diffusive transport from dilute towards enriched regions is impossible – it would violate the 2nd Law of Thermodynamics. Rather, non-diffusive transport by the viscous flow – driven by pressurization that is negligible in the context of Eq. (4) but nonzero nonetheless – is required to overcome inward O_2 diffusion and drive O_2 out of substomatal cavities. Diffusion of O_2 into substomatal cavities is massive, due to concentration differences of hundreds or thousands of ppm across the leaf's pore depth. Gradients and diffusion of O_2 exceed those of CO_2 by orders of magnitude.

However simplistic, the model improves upon the accuracy of previous assumptions regarding substomatal p_{O_2} that neglected Dalton's law. These include the assumption that p_{O_2} is a fixed parameter that does not depend substantially on plant functioning (Farquhar and Wong, 1984), as well as the notion that substomatal cavities are enriched in O_2 (Parkhurst, 1994), purporting outward O_2 diffusion while overlooking the dominant effects of transpiration on O_2 abundance. The greatest inaccuracies of the Daltonian model presented here can be bounded by considering the chief processes that it does not take into account.

Adhering to the principle of parsimony, the model neglects the effects of two lesser and partially offsetting influences on p_{O_2}, neither of which can alter the above conclusion regarding O_2 transport mechanisms. Firstly, photosynthetic O_2 production must reduce the O_2 pressure deficit, increasing substomatal O_2 somewhat, but certainly not by the many hundreds of ppm (or thousands for warm leaves) that would be required to make Δp_{O_2} positive. This seems clear when recalling the stoichiometric relation between O_2 and CO_2, and the trace amounts of the latter gas that limit the possible magnitude of photosynthetic Δp_{CO_2}. Secondly, molecular diffusion's discrimination among dry-air species must increase the O_2 deficit since N_2 (28 g mol^{-1}), representing 78.1% of atmospheric dry air molecules, diffuses upstream into substomatal cavities more rapidly than does O_2 (32 g mol^{-1}) according to Graham's law. Unaffected by these inaccuracies, the deduction that substomatal cavities generally are very dilute in O_2 is ineluctable, as is the conclusion that stomatal O_2 transport is predominantly non-diffusive. Specifically, it is due to an air jet that indiscriminately pushes all gases outwards (Kowalski, 2017).

At very high leaf *T*, these implications from gas physics become relevant to the behaviour of CO_2 and water vapour.

Regarding CO_2, non-diffusive transport cannot be neglected universally, since it neither discriminates among gas species nor depends on concentration gradients, unlike diffusion. The p_{O_2} model presented here is not valid for estimating p_{CO_2}, whose fluctuations are principally determined by photosynthesis. However, independent of photosynthetic drawdown (well, physically independent), the assumption of proportional depression of the partial pressures of dry air's components when supplanted by water vapour seems valid. Accordingly, just as Eq. (7) apportions 21% of supplanted dry air to O_2 depression, for a CO_2 concentration of 420 ppm we can expect 0.042% of the dry-air depression described by Eq. (4) to correspond to p_{CO_2}. This influence is negligible for temperate leaves with modest VPDs. For example, for the cool leaf in Table 1, it implies CO_2 depression of ~0.0001 kPa; near sea level, this is about 1 ppm and pales in comparison to photosynthetic drawdown. By contrast, for the warm leaf also near sea level, it means substomatal CO_2 depression by over 7 ppm, which is no longer negligible and drives inward CO_2 diffusion that is not due to photosynthesis. During heat waves, with extreme values of VPD, substomatal CO_2 depression due to humidification can be much larger. Thus, at very high leaf *T* non-diffusive transport can appreciably suppress photosynthesis via CO_2 limitation, but it has the opposite effect on transpiration.

Water vapour is also forced out of stomata by non-discriminating jets, with relevance that depends on water vapour abundance. Applying Newtonian physics to the momentum of air within stomata, Kowalski (2017) showed that the water vapour mass fraction, or specific humidity (q), defines the fraction of water vapour transport that is non-diffusive. Within substomatal cavities that are essentially saturated, the state variable q is largely determined by *T*. For the cool leaf in Table 1 ($q < 1\%$), non-diffusive transport can reasonably be neglected. But this is not so for the warm leaf ($q > 3\%$), and furthermore *q* increases rapidly as leaf *T* rises. If these increases in water vapour transport rates seem modest, versus what can be achieved by diffusion alone, they grow in importance when considered in combination with jet suppression of photosynthesis.

The consequences of gas physics at high leaf *T* are disparate for water vapour and CO_2 exchanges. Ejecting all gases, stomatal jets enhance water-vapour loss and oppose CO_2 ingress, boosting transpiration and suppressing photosynthesis versus the capabilities of diffusive transport alone. They thereby reduce water-use efficiency via effects on each gas. Thus far, the derivation of non-diffusive transport by stomatal jets has been little heeded by scientists who study leaf gas exchanges (De Kauwe et al., 2019; Vesala, 2024). However, dry-air depression and non-diffusive transport likely explain the decoupling of transpiration and photosynthesis that has been observed widely at very high leaf *T* (Aparecido et al., 2020; De Kauwe et al., 2019; Diao et al., 2024; Krich et al 2022; Marchin et al., 2023). In very hot substomatal cavities where water vapour is not a mere trace gas, jet transport casts doubt on the very meaning of stomatal conductance. And non-diffusive transport is gaining in relevance regarding leaf gas exchanges as the Earth warms and heatwaves increase in frequency and intensity (IPCC, 2021).

5 Conclusions

Water vapour's elevated partial pressure inside substomatal cavities implies depressed partial pressures of dry air components including oxygen (O_2), according to Dalton's law with negligible cavity pressurization. Substomatal cavities, not photosynthetically enriched in O_2, are dilute because of transpiration. Only non-diffusive conveyance can account for transport of O_2 from these O_2-poor cavities into the more aerobic, ambient atmosphere. Slight substomatal pressurization, however negligible in the context of Dalton's law, is sufficient to drive jets of air out of stomatal apertures. The relevance of stomatal jets to gas transport cannot be neglected universally in plant physiology, becomes important for water vapour and CO_2 in leaves at very high *T*, and therefore is increasing with global warming.

Competing interests

The author declares that he has no competing interests.

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