

**Redox Addressing:
Finite Memory and the Cost of Symmetry in Multielectron
Catalysis**

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Abstract

A catalyst that must store m oxidizing equivalents before a product forms loses progress whenever a stored equivalent decays, and N equivalent catalytic sites that share a stream of holes at random each see only a fraction of it. For a site that needs m hits and loses each stored step at rate μ , the product flux is $J = r / \sum_{j=0}^{m-1} (m-j)(\mu/r)^j$ when holes arrive at rate r , and N unbiased sites at memory rate μ have exactly the flux of one addressed site at rate $N\mu$: symmetry costs a factor N in memory lifetime. The penalty is a weighted mean of N^j that rises monotonically as the memory number $M = \lambda/\mu$, holes per memory lifetime, falls, from 1 in strong light to N^{m-1} in weak light, a limit shared by three loss mechanisms. For $N = 2$ and $m = 4$ it is 8 in weak light and 2.60 at one hole per memory lifetime, and symmetry costs less than 10% only above 8.66 holes per lifetime. Recovering 90% of the one-site flux at one hole per lifetime needs a routing bias of 0.95, or state-dependent routing that favors the more advanced site by about 2 log-odds per stored equivalent. Routing that favors the less advanced site, as a redox-potential argument would suggest, falls below random routing and changes the weak-light exponent from m to $2m-1$. Damage concentrated in the most oxidized state is exactly N times larger per product for N symmetric sites at every light level. In Photosystem II the model gives the heterodimer a flux advantage only if the ancestral memory number was below about 9, and it names what a two-sided photosystem must be measured for: the routing probability as a function of the two sites' states, which a flash-interval series separates, with yield ratios of 0.32, 0.79, 0.97 and 0.01 against one site at a flash interval of 0.83 memory lifetimes.

1. Four oxidations and two possible sites

Photosystem II (PSII) oxidizes water by accumulating four oxidizing equivalents at a Mn_4CaO_5 cluster. The four photochemically formed equivalents cooperate within one reaction centre, S_0 and S_1 are stable in the dark and S_2 and S_3 are not (Kok et al. 1970), and the steps between them are part of an eight-step cycle of alternating electron and proton removal (Dau and Haumann 2007). Each light-driven step has a miss probability that depends on the S state, from 0% to 23% depending on the transition and the temperature (Han et al. 2012, 2022). Recombination reactions that drain stored oxidizing equivalents are a general property of reaction centres and have been proposed to protect against oxygen chemistry at the price of efficiency (Rutherford et al. 2012; Vass 2011). Repair of PSII replaces damaged subunits selectively, predominantly D1 (Nixon et al. 2010).

The core of PSII is a heterodimer of D1 and D2, and the cluster sits on the D1 and CP43 side (Umena et al. 2011; Suga et al. 2015). On the D2 side four phenylalanines fill the cavity where the cluster sits in D1, two of them at positions homologous to the D1 ligands D170 and E189, and metal was probably coordinated on both sides of the early symmetric complex (Cardona et al. 2015). Ancestral sequence reconstruction supports water oxidation before the duplications that produced the core antenna subunits (Oliver et al. 2021), a review places its origin long before the diversification of cyanobacteria (Oliver et al. 2023), and the origin of the cluster has been described as the transformation of an ancestral reaction centre (Cardona 2016). Duplication of a homomeric complex generally yields a heteromeric complex of paralogs (Pereira-Leal et al. 2007). Rutherford

and Faller proposed that a highly oxidizing homodimeric ancestor would have been inefficient in photochemistry and charge storage and wasteful through oxidative damage, and that these problems selected the lopsided heterodimer in which the highly oxidized species are limited to one side (Rutherford and Faller 2003). Calculations assign about 80% of the cation of the chlorophyll pair to the D1 side, a bias produced by the same D1/D2 residue pairs that differ at the metal ligand positions (Saito et al. 2011), and in Mn-depleted PSII TyrD can donate to the oxidized pair when TyrZ is absent, which needs partial localization of the cation on the D2 side (Faller et al. 2001); its slow oxidation in intact PSII reflects proton movement near the tyrosine (Saito et al. 2013).

The charge-storage half of that proposal is qualitative. Two catalytic sites that receive the holes at random each advance at half the rate, and a site that stalls loses its stored equivalents. We ask how large the cost is, how it depends on the number of equivalents and on the light, and which routing rules remove it. We call the assignment of each successive hole to one site addressing, as one writes to an address; the word is a mnemonic. The sources listed in sources.md contain no expression for the flux of N symmetric accumulators as a function of the memory number. The sums below are elementary and the closed form may be known in other fields.

The results are as follows. The flux of one site has a closed form, and N unbiased sites at memory rate μ reproduce one addressed site at rate $N\mu$ for every loss mechanism with a single rate scale. The penalty of symmetry is a weighted mean of N^j , bounded by N^{m-1} , monotone in the memory number, and equal to N^{m-1} in weak light for stepwise, independent and collective loss alike. A fixed routing bias and positive state-dependent routing both remove most of the penalty at moderate bias; negative state-dependent routing is worse than none. Damage in the top state is N times larger per product at every light level. A flash-train experiment on a two-sided photosystem separates these routing rules, and its identity of two sites with one attenuated site is parameter free.

2. The model

Holes arrive at a reaction centre as a Poisson stream of rate λ and are routed to one of N catalytic sites, to site i with probability p_i , which may depend on the states of the sites. A site holds $s \in \{0, \dots, m-1\}$ stored equivalents. A hole at a site in state $s < m-1$ raises s by 1. A hole at a site in state $m-1$ yields one product and resets the site to 0. Stored steps are lost at a rate set by one parameter μ . In the main model loss is stepwise: $s \rightarrow s-1$ at rate μ for every $s \geq 1$. Independent loss ($s \rightarrow s-1$ at rate $s\mu$) and collective loss ($s \rightarrow 0$ at rate μ) serve as checks. The memory lifetime is $\tau = 1/\mu$ and the memory number is $M = \lambda/\mu = \lambda\tau$, the number of holes that arrive per memory lifetime. The product flux J is the long-run rate of product events, and $mJ \leq \lambda$.

Water oxidation has $m = 4$, one-electron chemistry such as the oxidation of Mn^{2+} has $m = 1$, and chemistry at the peroxide level has $m = 2$. The stored quantity counts oxidizing equivalents; the protons that accumulate with them in the eight-step cycle (Dau and Haumann 2007) are not tracked. With routing independent of the states, thinning of the Poisson stream gives each site an independent Poisson stream of rate λp_i (Cox and Isham 1980).

Every flux reported below is the stationary flux of the Markov chain on the m^N states of the sites, computed with the subtraction-free GTH algorithm (Grassmann et al. 1985), which stays accurate at the tiny occupation probabilities of weak light. Five cases were also simulated by uniformization, an exact stochastic simulation in the sense of Gillespie (Gillespie 1977).

3. Exact results

3.1 One site

Proposition 1. A site that receives holes at rate r and loses stored steps stepwise at rate μ has product flux

$$J_1(r, \mu) = \frac{r}{\sum_{j=0}^{m-1} (m-j)(\mu/r)^j}.$$

Proof. The site returns to state 0 after every product, so product times form a renewal process and J_1 is the reciprocal of the mean time T from state 0 to the next product (Norris 1997). Let d_s be the mean time to go from state s to state $s+1$, where state m stands for the product. From state 0 the next event is a hole at rate r , so $d_0 = 1/r$. From $s \geq 1$ the site waits for a time with mean $1/(r+\mu)$, advances with probability $r/(r+\mu)$, and otherwise falls to $s-1$ and must climb back, so $d_s = 1/(r+\mu) + \mu(d_{s-1} + d_s)/(r+\mu)$, which gives $d_s = 1/r + (\mu/r) d_{s-1}$ and $d_s = r^{-1} \sum_{j=0}^s (\mu/r)^j$. Summing over s from 0 to $m-1$ gives $T = r^{-1} \sum_{j=0}^{m-1} (m-j)(\mu/r)^j$. $\square$

In strong light ($r \gg \mu$) the sum approaches m and $J_1 \rightarrow r/m$, every hole being used. In weak light the term $j = m-1$ dominates and $J_1 \rightarrow r^m/\mu^{m-1}$.

3.2 Symmetric sites

Proposition 2. With state-independent routing $p_i = 1/N$ the flux of N sites at memory rate μ equals the flux of one site that receives all the holes at memory rate $N\mu$: $J_N(\lambda, \mu) = J_1(\lambda, N\mu)$.

Proof. Thinning gives N independent sites, each with hole rate λ/N , so $J_N(\lambda, \mu) = NJ_1(\lambda/N, \mu)$. By Proposition 1, $J_1(r, \mu) = \mu \varphi(r/\mu)$ with $\varphi(a) = a / \sum_j (m-j)a^{-j}$. Then $NJ_1(\lambda/N, \mu) = N\mu \varphi(\lambda/N\mu) = J_1(\lambda, N\mu)$. $\square$

The proof uses only that the flux of one site is μ times a function of r/μ , which holds for any loss mechanism whose rates all scale with μ ; the identity therefore holds for independent and collective loss as well. Symmetry costs a factor N in memory lifetime at every light level.

Corollary 1. The penalty $\Pi_N = J_1(\lambda, \mu)/J_N(\lambda, \mu)$ is

$$\Pi_N(M) = \frac{\sum_{j=0}^{m-1} (m-j)(N/M)^j}{\sum_{j=0}^{m-1} (m-j)(1/M)^j} = \sum_{j=0}^{m-1} w_j N^j, \quad w_j = \frac{(m-j)M^{-j}}{\sum_k (m-k)M^{-k}},$$

a weighted mean of N^j . It satisfies $1 \leq \Pi_N \leq N^{m-1}$, decreases monotonically as M rises, tends to N^{m-1} as $M \rightarrow 0$ and to 1 as $M \rightarrow \infty$.

Proof. The expression follows from Propositions 1 and 2. The weights are positive and sum to 1, which gives the bounds. With $y = 1/M$ the ratio $w_{j+1}/w_j = y(m-j-1)/(m-j)$ increases with y , so the distribution of j is stochastically increasing in y ; N^j increases with j , so the mean increases with y . The limits follow from the concentration of the weights on $j = m-1$ as $y \rightarrow \infty$ and on $j = 0$ as $y \rightarrow 0$. $\square$

For $m = 2$ the penalty is $(2 + N/M)/(2 + 1/M)$. For $N = 2$ and $m = 4$ it is $26/10$ at $M = 1$.

3.3 The weak-light law and the trapping probability

Proposition 3. Suppose every state $s \geq 1$ is left downward at a rate $\ell_s > 0$. Then $J_1(r) = c r^m (1 + O(r))$ with $c = \prod_{s=1}^{m-1} \ell_s^{-1}$, and the penalty of N unbiased sites tends to N^{m-1} as $M \rightarrow 0$.

Proof. Balance the flow across the cut between states $\{0, \dots, s-1\}$ and $\{s, \dots, m-1\}$: upward flow $r\pi_{s-1}$ equals downward flow $\ell_s \pi_s$ plus smaller terms, namely the downward flow from states above s , of order r^{s+1} , and the return flow $r\pi_{m-1}$ of order r^m , which is smaller than r^s for $s \leq m-1$. Hence $\pi_s = (r/\ell_s)\pi_{s-1}(1 + O(r))$, $\pi_{m-1} = r^{m-1} \prod_s \ell_s^{-1}(1 + O(r))$ and $J_1 = r\pi_{m-1}$. Then $NJ_1(\lambda/N)/J_1(\lambda) \rightarrow N^{1-m}$. $\square$

The constant c is μ^{1-m} for stepwise and collective loss and $\mu^{1-m}/(m-1)!$ for independent loss. Weak light makes the flux a power law of the hole rate with exponent m , and the symmetric penalty is a prefactor of the same law.

Corollary 2. If a hole becomes a stored equivalent with probability ρ and is otherwise lost, thinning drives the sites at rate $\rho\lambda$. The flux and the penalty depend on $\rho\lambda/\mu$ only. In weak light halving ρ divides the flux by 2^m .

The first Mn^{2+} oxidation during photoassembly of the cluster is slow and endergonic, and proton transfer to D1-H332 supplies the driving force (Watanabe and Noguchi 2026); the dark rearrangement that follows the first flash involves protein conformational changes and relocation of Mn^{3+} (Kato et al. 2025). A trapping probability $\rho < 1$ is therefore a physical quantity, and an improvement of ρ and an improvement of τ are interchangeable in the penalty. Apo-PSII forms extended Mn(III,IV) oxide particles with 50 to 100 Mn per photosystem (Chernev et al. 2020), and photoactivation is reviewed in Bao and Burnap (2016); those processes set the sites and are outside the model.

4. Routing, damage and the number of stored equivalents

4.1 Checks

The closed form of Proposition 1 agrees with the stationary flux of the full chain for random parameter sets with m from 1 to 5, the identity of Proposition 2 and the thinning identity agree with the chain for $N = 2$ and $N = 3$, and the identity also holds for independent and collective loss, all

to machine precision. The weighted-mean form agrees with the direct ratio of fluxes for m from 2 to 5 and N from 2 to 4, and the penalty is monotone and within its bounds on a grid of M from 10^{-3} to 10^3 . Simulations by uniformization agree with the exact flux of the chain in all five cases tested, with a largest deviation of 1.45 standard errors (Figure 1).

In weak light the slope of $\log J$ against $\log M$ is 4.00 for $m = 4$ under stepwise and independent loss and 3.99 under collective loss, and the penalty approaches 7.99, 7.99 and 7.98 against $N^{m-1} = 8$ at $M = 0.001$ (Figure 2d).

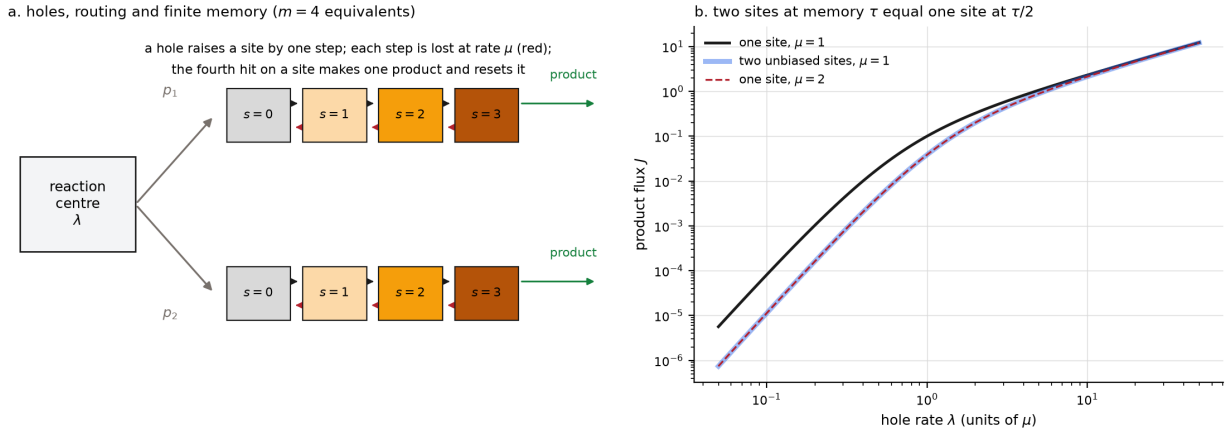


Figure 1: The model and the rescaling identity. (a) Holes reach a reaction centre at rate λ and are routed with probabilities p_i to sites that hold up to $m - 1$ stored equivalents; each step is lost at rate μ and the m -th hit gives a product. (b) Product flux against hole rate for one site at $\mu = 1$, two unbiased sites at $\mu = 1$ (computed from the full chain) and one site at $\mu = 2$; the last two coincide.

4.2 The size of the penalty

At one hole per memory lifetime ($\lambda = \mu = 1$, $m = 4$) a single site yields 0.100 products per unit time and two unbiased sites yield 0.0385, a ratio of 2.60; the closed forms are $1/10$ and $1/26$. Table 1 gives the penalty of two sites for m from 1 to 4. At $m = 1$ a hole yields a product at once and symmetry costs nothing. At $m = 4$ the penalty is 7.18 at $M = 0.1$, 2.60 at $M = 1$ and 1.08 at $M = 10$.

Table 1: Penalty Π_2 of two unbiased sites against the number m of stored equivalents and the memory number M .

m	$M = 0.1$	$M = 1$	$M = 10$
1	1.00	1.00	1.00
2	1.83	1.33	1.05
3	3.60	1.83	1.07
4	7.18	2.60	1.08

Table 2 gives the memory number above which the penalty is at most 1.1. For $N = 2$ and $m = 4$ it is 8.66: symmetry costs less than 10% only when more than 8.66 holes arrive per memory lifetime. The geometric midpoint of the range of the penalty, $\Pi = 2^{3/2}$, is reached at $M = 0.90$.

Table 2: Memory number M above which the penalty of N unbiased sites is at most 1.1.

N	$m = 2$	$m = 3$	$m = 4$
2	4.50	7.32	8.66
3	9.50	14.48	16.83
4	14.50	21.63	24.98

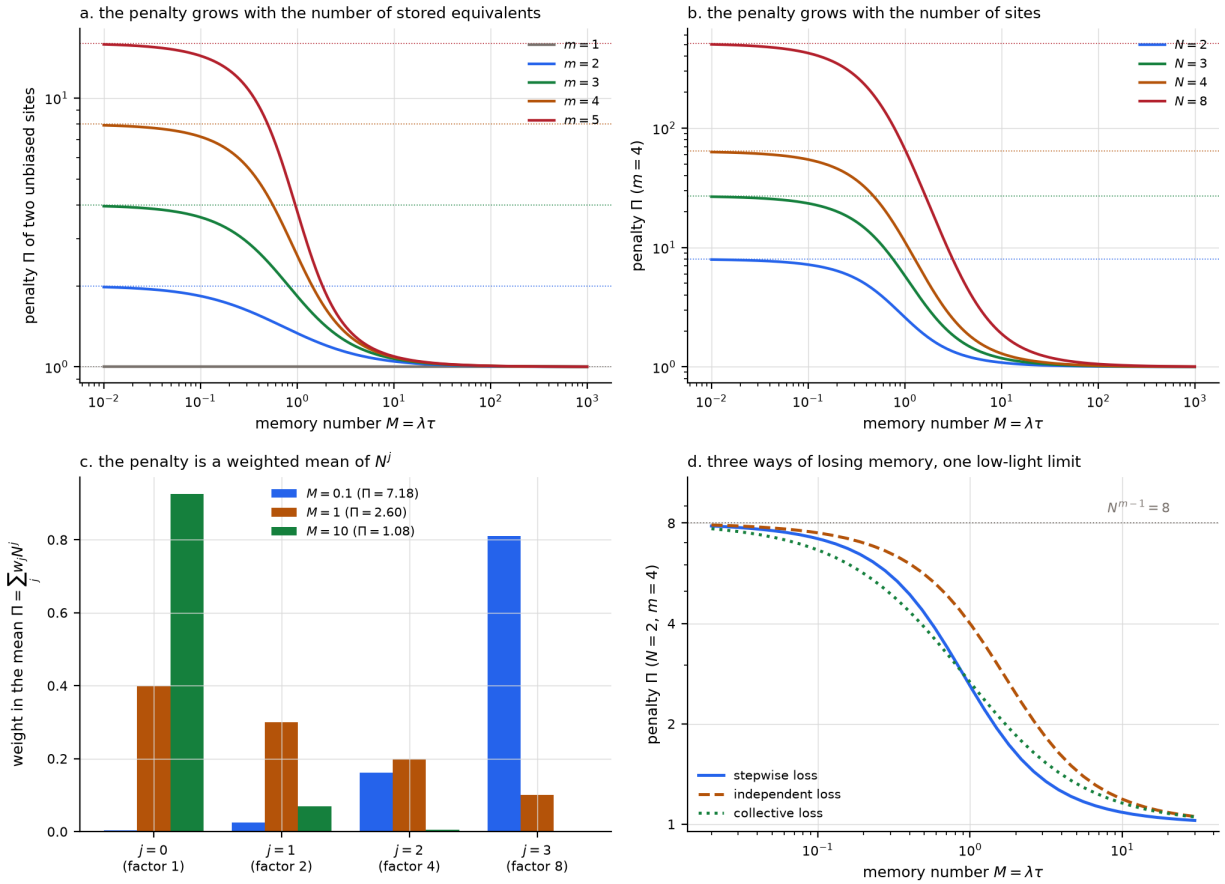


Figure 2: Penalty of symmetry. (a) Penalty of two unbiased sites against the memory number M for m from 1 to 5; dotted lines mark 2^{m-1} . (b) The same for N from 2 to 8 at $m = 4$; dotted lines mark N^3 . (c) Weights of the weighted mean $\Pi = \sum_j w_j N^j$ for $N = 2$ and $m = 4$ at three memory numbers. (d) Penalty under stepwise, independent and collective loss ($N = 2$, $m = 4$), which share the weak-light limit.

4.3 Fixed asymmetry

Let site 1 receive a fraction p of the holes. By thinning, $J(p) = J_1(p\lambda, \mu) + J_1((1-p)\lambda, \mu)$. At $M = 0.1$ a routing probability of 0.98 recovers 90% of the flux of one addressed site, at $M = 0.3$ it takes 0.97, at $M = 1$ it takes 0.95 and at $M = 3$ it takes 0.93; at $M = 10$ unbiased routing already gives 92% of the one-site flux (Figure 3a). The calculated 80:20 distribution of the cation over the chlorophyll pair (Saito et al. 2011) would, if it set the routing between two active sites, recover 0.43, 0.48, 0.63, 0.80 and 0.93 of the one-site flux at $M = 0.1, 0.3, 1, 3$ and 10. That distribution is the charge over the pair, and the routing between catalytic sites is a different quantity; the numbers show how much of the penalty a bias of that size would remove.

4.4 State-dependent routing

Let the next hole go to site i with probability proportional to $\exp(\gamma s_i)$, so that $\gamma > 0$ favors the more advanced site and $\gamma < 0$ the less advanced one. For two sites and $m = 4$ the chain has 16 states. As $\gamma \rightarrow \infty$ the leader receives every hole, the second site is never occupied, and the flux equals that of one site. At $M = 1$ the flux relative to one site is 0.787 at $\gamma = 1$, 0.931 at $\gamma = 2$ and 0.976 at $\gamma = 3$, against 0.38 for unbiased routing. A value of $\gamma = 2.5$ recovers 90% of the one-site flux at every M from 0.1 to 3 (Figure 3b). A log-odds of 2.5 per stored equivalent is a modest cooperativity, and where it would come from, in a photosystem with one reaction centre and two donor sites, is an open physical question.

Negative feedback is far worse than random routing. At $M = 1$ the relative flux is 0.12 at $\gamma = -1$ and 0.07 at $\gamma = -3$; at $M = 0.1$ it is 0.0029 and 0.0001, against 0.14 for unbiased routing. For $\gamma \rightarrow -\infty$ the sites advance in step and a product needs $2m - 1$ holes within the memory, which gives a weak-light slope of 7.00 against 4.00 (Figure 3c). A site that has stored more positive charge is harder to oxidize further if electrostatics alone decides, and that argument gives $\gamma < 0$. The proton release that accompanies the S-state transitions (Dau and Haumann 2007) weakens it, and no measurement of the sign has been reported in the sources we examined.

4.5 Damage

Let the hazard of oxidative damage be d while a site is in its most oxidized state $s = m - 1$ and zero otherwise.

Proposition 4. With stepwise or independent loss, a site that receives holes at rate r spends a mean time $1/r$ in its top state per product, so damage per product is d/r . For N unbiased sites $r = \lambda/N$ and damage per product is Nd/λ , N times that of one site, at every M .

Proof. Each visit to the top state lasts for a time with mean $1/(r + \ell)$ and ends in a product with probability $r/(r + \ell)$, where ℓ is the loss rate from that state. A product therefore follows $(r + \ell)/r$ visits on average, and the time spent in the top state per product is $1/r$. $\square$

For a hazard that rises as e^s the damage per product is 7.25 times larger for two sites than for one at $M = 0.05$ and 2.01 times larger at $M = 50$ (Figure 4a). Per hole, that is for the same light, the

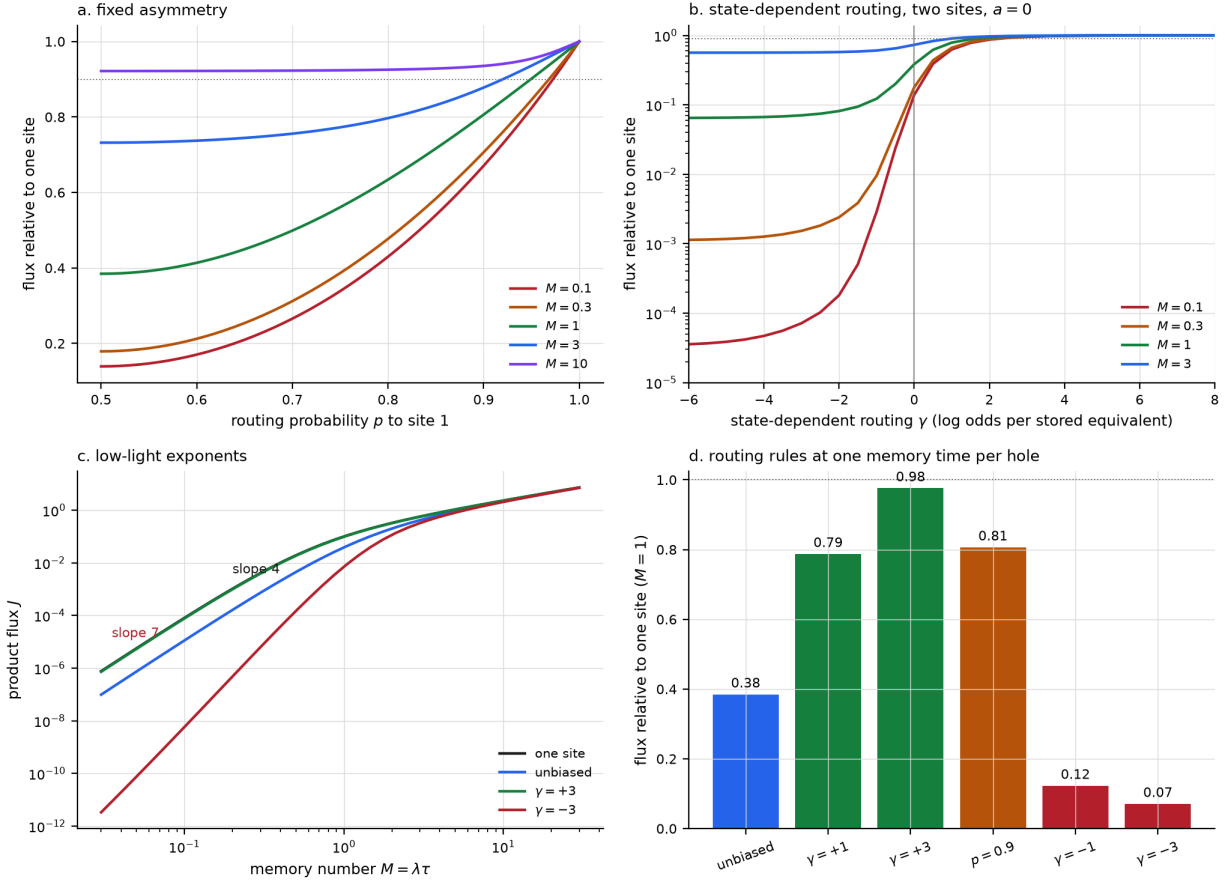


Figure 3: Routing rules for two sites ($m = 4$). (a) Flux relative to one site against the fixed routing probability p at five memory numbers. (b) Relative flux against the state-dependent routing parameter γ ; dotted line at 0.9. (c) Product flux against memory number for one site, unbiased routing, $\gamma = +3$ and $\gamma = -3$; the weak-light slopes are 4 and 7. (d) Relative flux of six routing rules at $M = 1$.

damage rate of two sites is below that of one at weak light and approaches twice that of one in strong light: for a top-state hazard the ratio is 0.26 at $M = 0.05$ and 1.97 at $M = 50$ (Figure 4b). Per product, the damage penalty did not fall below N for either hazard, so the damage argument for asymmetry holds at every light level if damage is concentrated in the top state, while the flux argument disappears above about $M = 9$. A selection curve with a minimum in between is not a result of this model. Whether the combined cost is U-shaped depends on the relative cost of damage and of lost product, which the model does not fix.

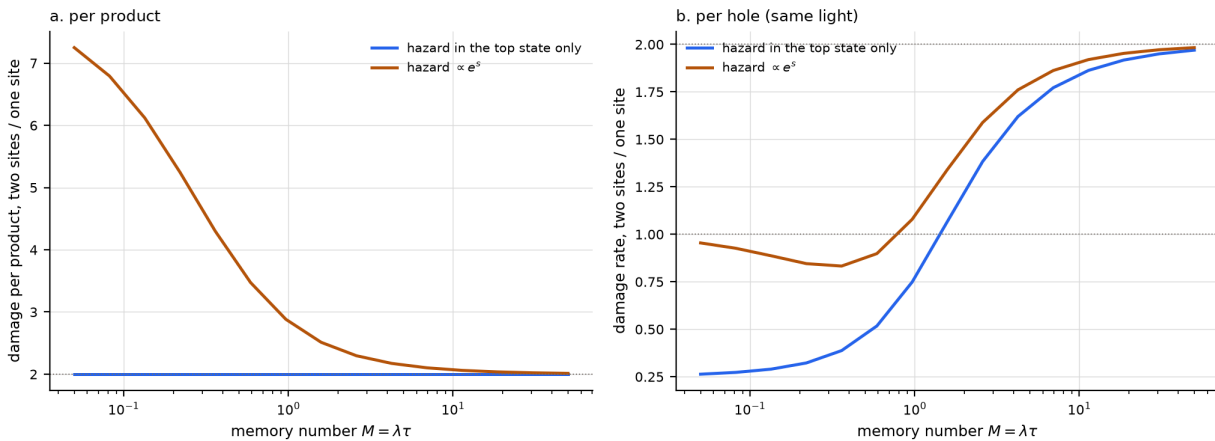


Figure 4: Damage. (a) Damage per product of two unbiased sites relative to one site, for a hazard in the top state only and a hazard proportional to e^s , against the memory number. (b) Damage rate per hole for the same two hazards; dotted lines at 1 and 2.

4.6 The number of stored equivalents

The weak-light penalty is N^{m-1} , which grows exponentially with m : 1, 2, 4 and 8 for $N = 2$ and m from 1 to 4. At one hole per memory lifetime it grows from 1.00 at $m = 1$ to 1.33, 1.83 and 2.60. A symmetric reaction centre that serves one-electron chemistry pays nothing, and the cost rises as the chemistry moves toward four-electron water oxidation. If memory then improved, the flux advantage of asymmetry would fall (it vanishes above $M = 9$ for $N = 2$ and $m = 4$) without removing the architecture; an improvement of memory by a factor N compensates symmetry (Proposition 2). Both statements concern the model. Whether the sequence record can date the rise of m relative to the improvement of memory is a separate question.

5. A flash experiment on a two-sided photosystem

A flash train delivers one hole per flash at intervals Δt , routed by the same rules, with stored steps lost between flashes. Let Y be the stationary mean number of products per flash. At short intervals one site yields 0.244 products per flash, close to $1/m$. For N unbiased sites the yield is N times that of one site whose flashes are attenuated to hit with probability $1/N$, because each site sees a thinned train and expectations add; the identity holds to numerical precision on the grid

of intervals tested. It is an experimental prediction without a free parameter: measure one site at attenuated flash energy and predict the two-sided yield.

At long intervals the yield of two unbiased sites approaches, numerically, $2^{-(m-1)}$ of the yield of one, 0.125 at $m = 4$. At a flash interval of 0.83 memory lifetimes ($\mu\Delta t = 0.83$) the yield of one site is 0.093 per flash, and the yields of two sites relative to it are 0.32 for unbiased routing, 0.79 for a fixed bias of 0.9, 0.97 for $\gamma = +3$ and 0.01 for $\gamma = -3$ (Figure 5). The four routing hypotheses are separated by a single interval. If flash outcomes were independent trials, a 10% relative standard error of the yield would take 976 flashes for one site, 3,298 for two unbiased sites, 1,265 for a bias of 0.9, 1,005 for $\gamma = +3$ and 88,869 for $\gamma = -3$. Correlation between successive flashes raises these numbers. A direct simulation of flash trains agrees with the matrix solution.

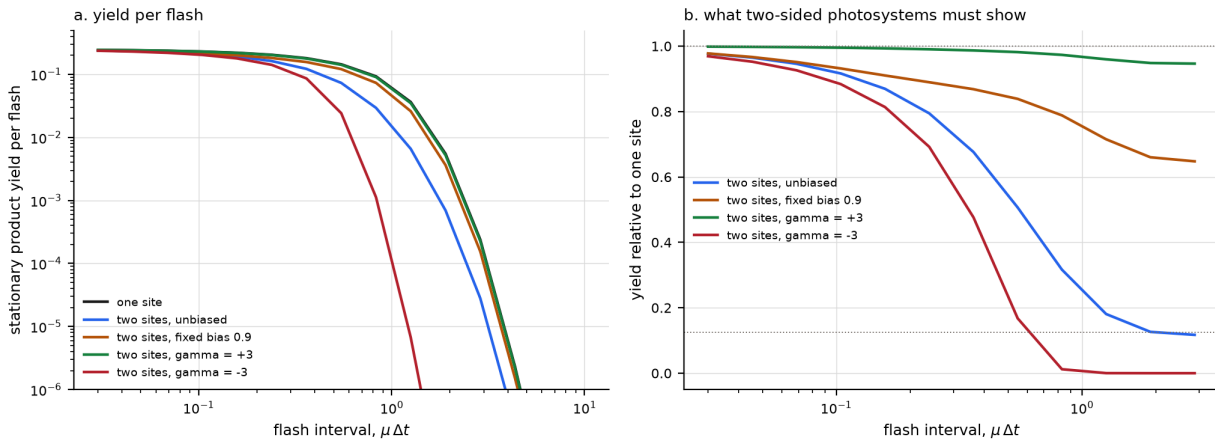


Figure 5: Flash trains. (a) Stationary product yield per flash against the flash interval $\mu\Delta t$ for one site and for two sites under four routing rules. (b) Yield of two sites relative to one site; dotted lines at 1 and at 2^{-3} .

The quantity that decides between the routing rules is the routing probability as a function of the states of the two sites, $p_1(s_1, s_2)$. Fixed asymmetry gives a constant, positive feedback an increasing function of $s_1 - s_2$, and negative feedback a decreasing one. The model identifies a measurement; whether a photosystem with two active donor sites can be built, for example by reversing the substitutions that disable the D2 side, is an experimental question that the paper does not address.

The finite-memory account of the heterodimer is refuted for a given ancestral reconstruction if the memory number of its donor-side chemistry exceeds about 9 at the irradiance of its habitat, since then symmetry costs less than 10% of the flux. It is refuted as a selective explanation for the D2 side if a two-sided construct shows state-dependent routing of 2.5 log-odds per stored equivalent or more, which recovers 90% of the one-site flux from $M = 0.1$ to $M = 3$. It survives, and acquires an estimate of γ , if the measured routing is close to unbiased or negative.

6. Limits

The model has Poisson hole arrivals, equal sites, state-independent loss rates and routing in a one-parameter family, and no saturation of the reaction centre: the product flux can reach λ/m however fast the holes arrive, while a real centre has a turnover limit. Loss is modeled as one rate; in PSII the loss of stored equivalents depends on recombination with reduced acceptors and on the S state (Rutherford et al. 2012; Han et al. 2012), and the miss parameters of modern PSII are a mixture of these processes. Proposition 3 covers any loss mechanism in weak light, and the identity of Proposition 2 any mechanism with a single rate scale, but the numerical results in the middle range are for the three mechanisms named. The model counts oxidizing equivalents and ignores the accumulation of protons and the conformational states of the cluster, and the damage hazard is an assumed function of the state.

The paper does not show that the D1/D2 asymmetry arose for these reasons. It gives the cost of symmetry as an exact function of the memory number, shows that the cost is a factor N in memory lifetime and N^{m-1} in weak-light flux, identifies the routing rules that remove it and the one that makes it worse, and states two measurements that would test whether a two-sided photosystem needs the asymmetry it has. The memory number of an ancestral donor side is not known, and the model makes the statement that depends on it explicit: above about 9 holes per memory lifetime the flux argument has no force.

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