Organic Oxidation Mechanisms

and

Organic Aerosol

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on

Atmospheric Chemical Mechanisms

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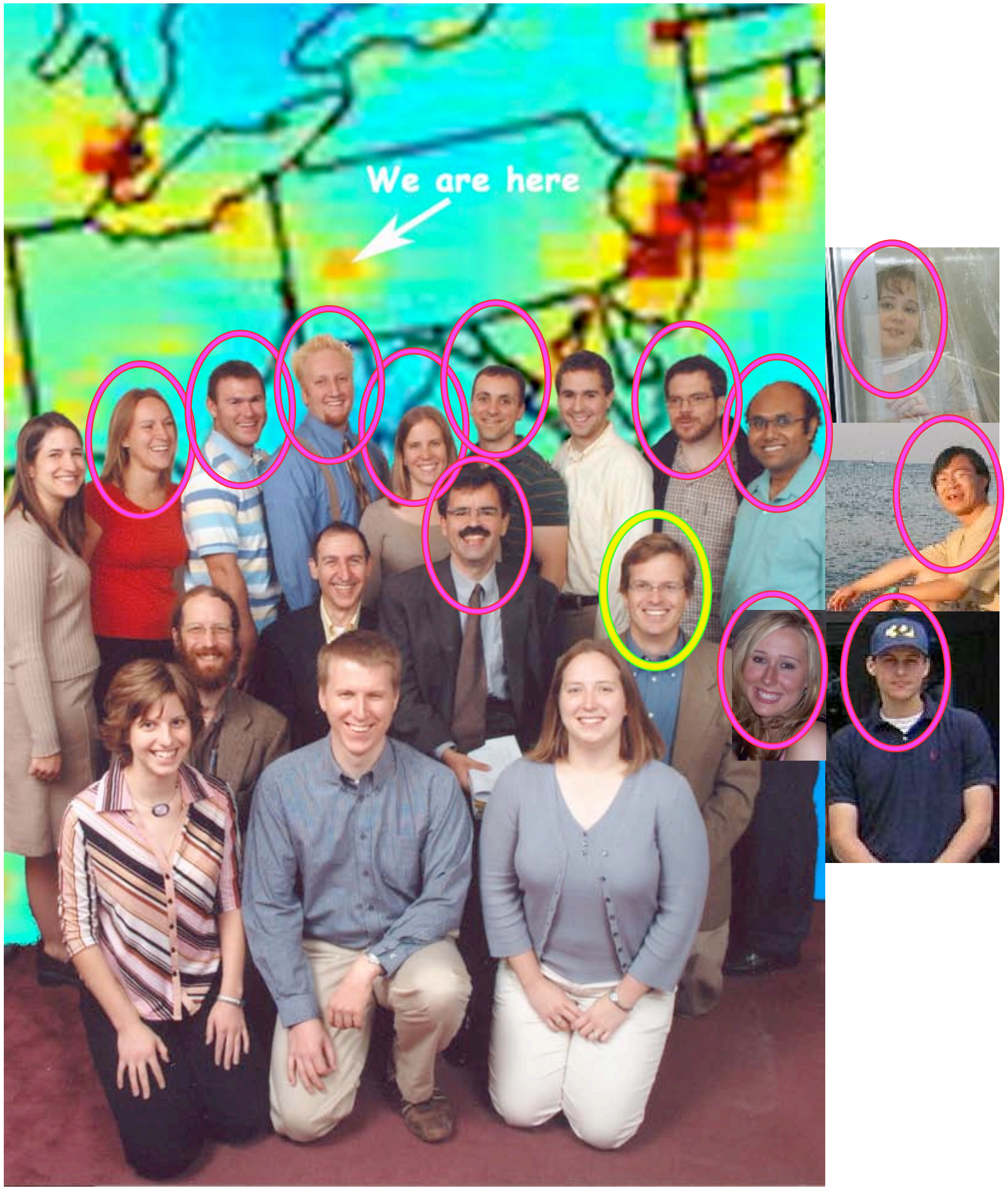
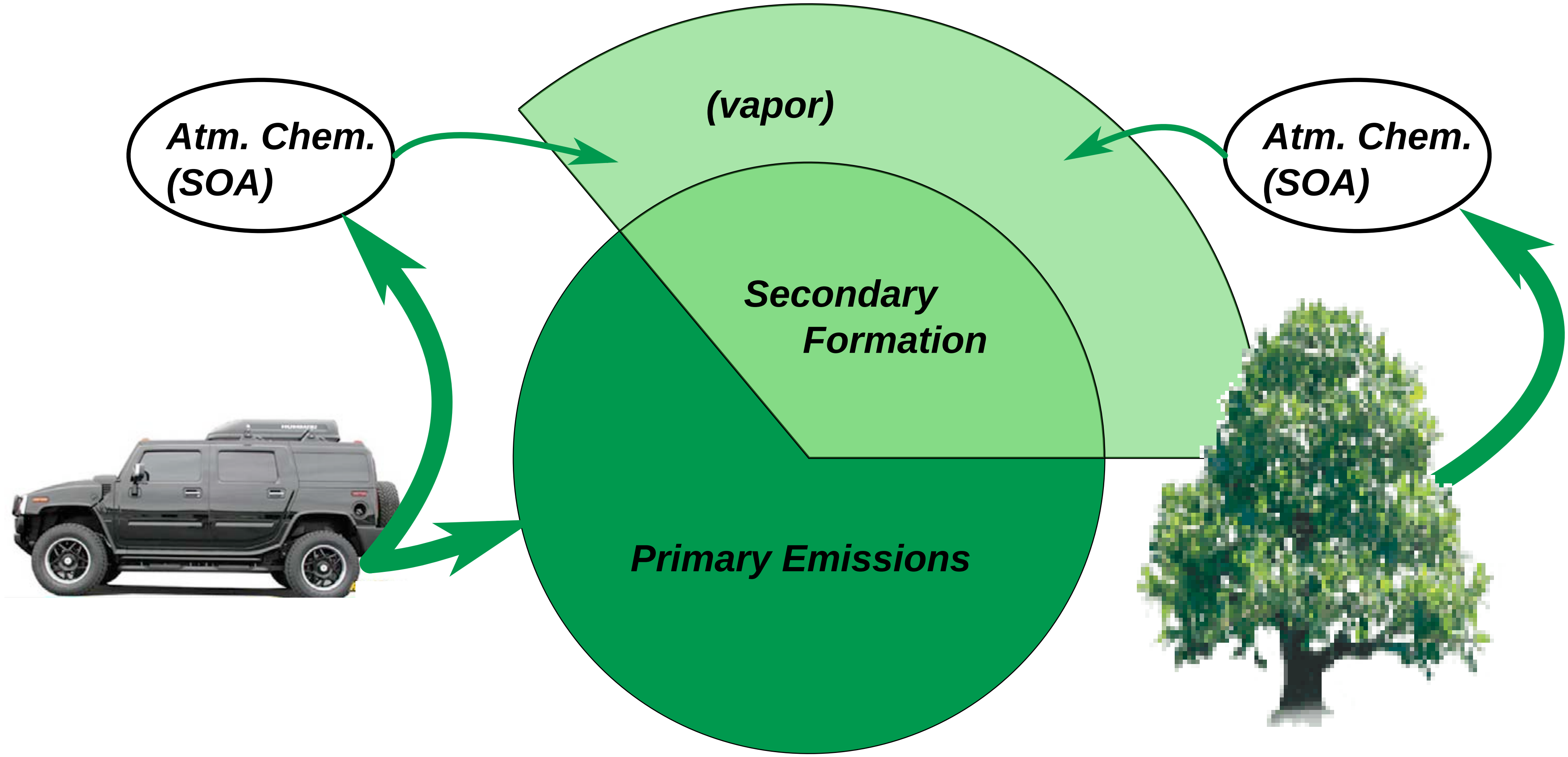
The Center for Atmospheric Particle Studies

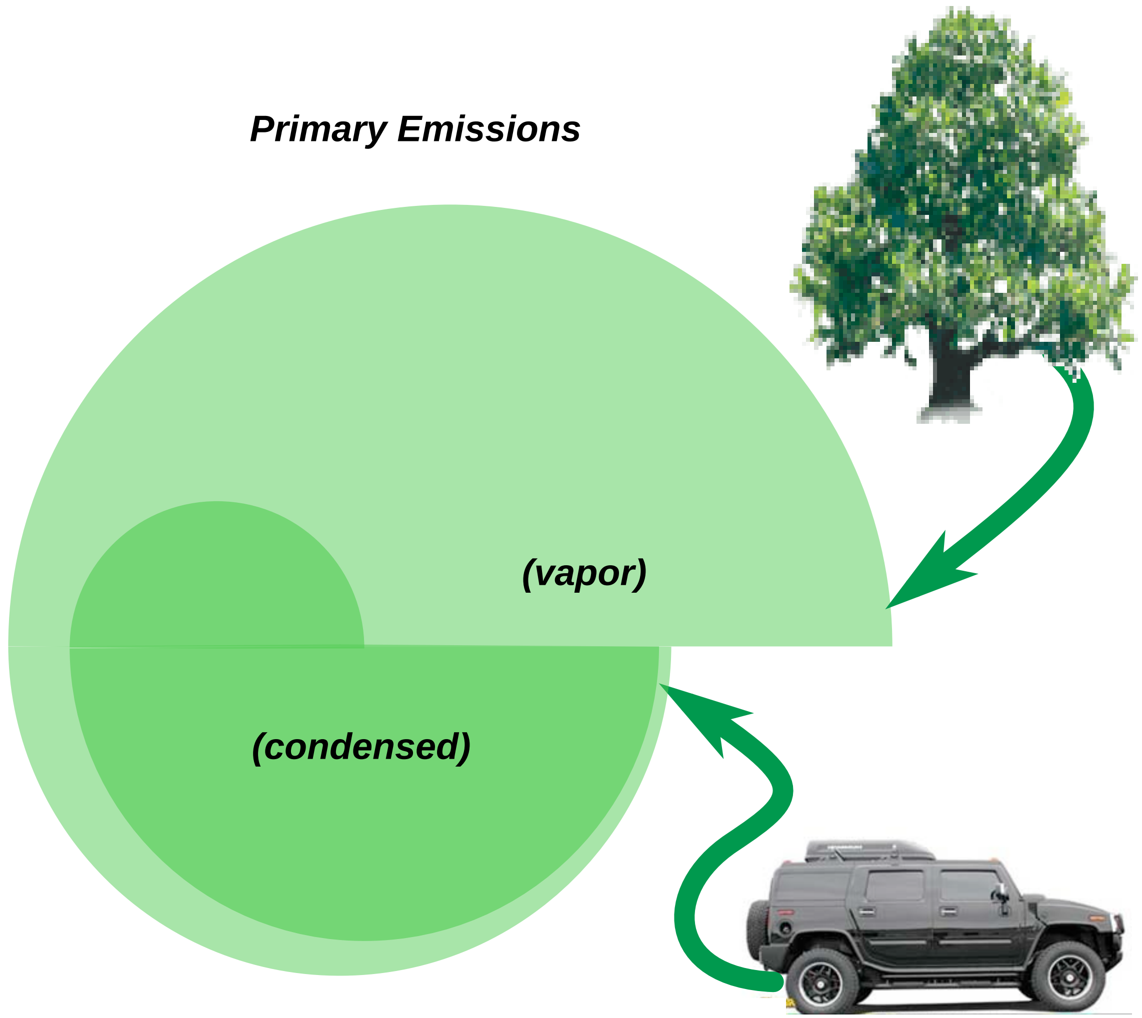


Old View: Primary and Secondary OC



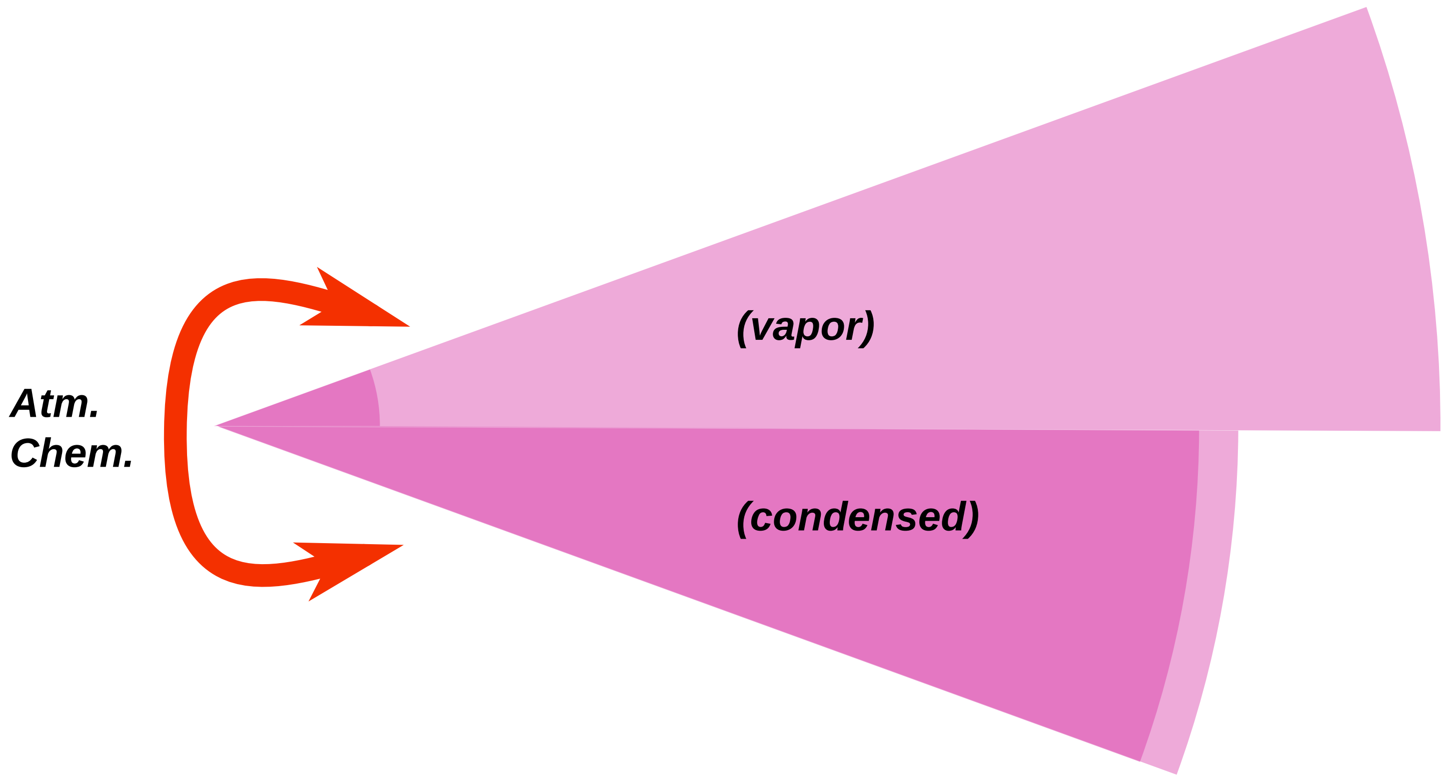
- Primary emissions from human sources – nonvolatile.
- Secondary production mostly biogenic?? – semivolatile.

New View: Semivolatile Primary Emissions



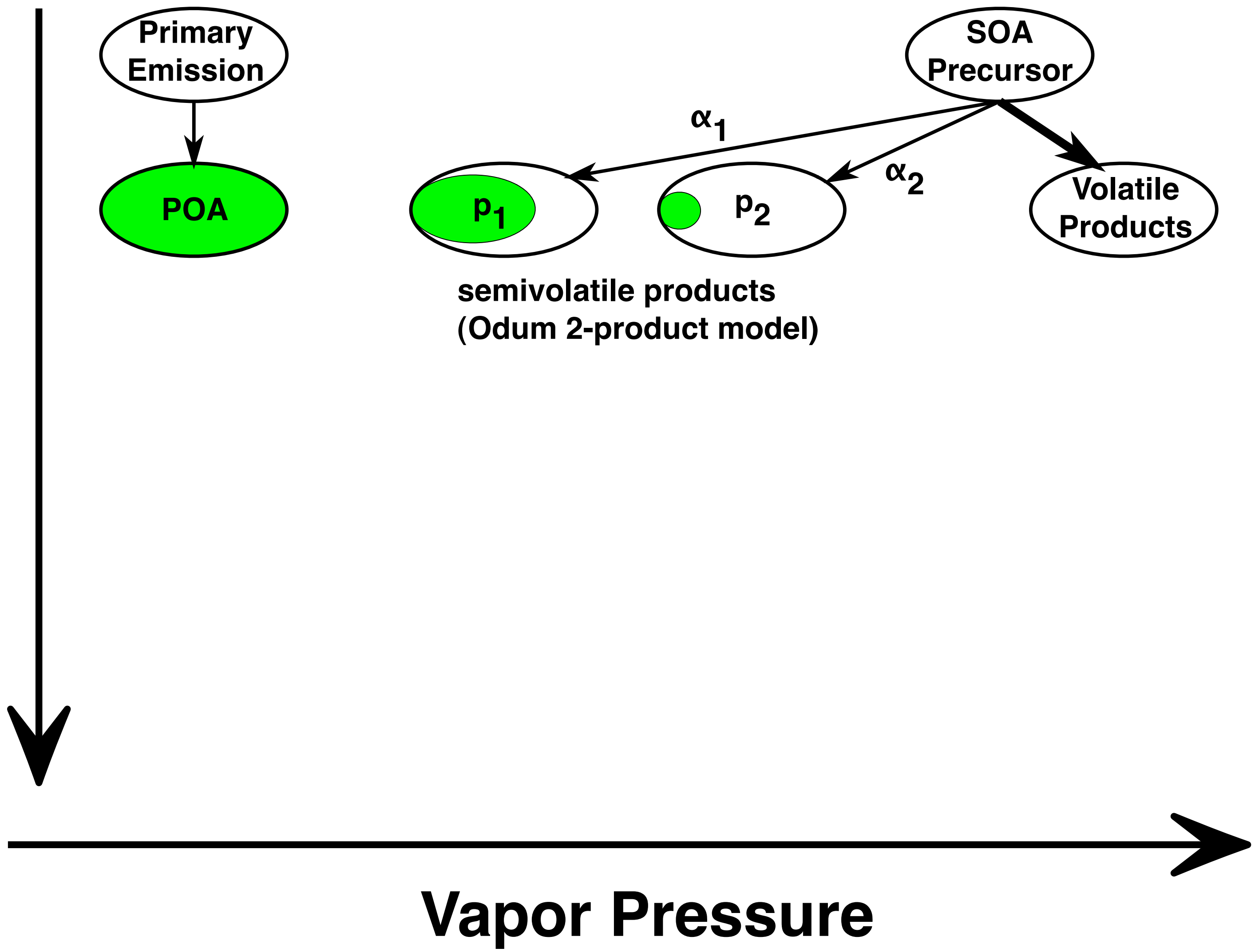
- Primary emissions from human sources – lower volatility.
- Primary emissions from biogenic sources – higher volatility.

New View: Atmospheric Chemistry



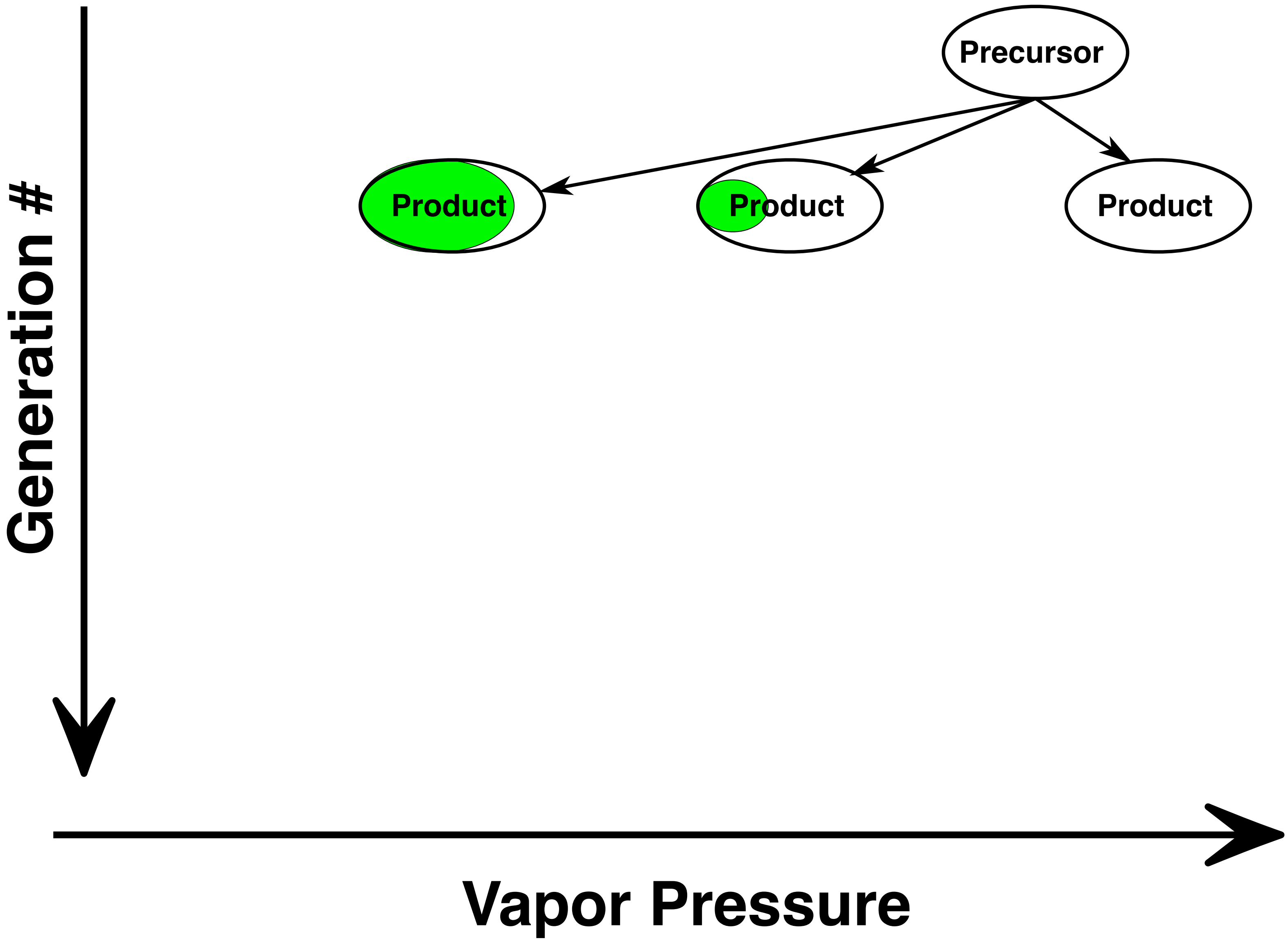
- Chemistry in all phases drives material toward extremes.

Organic Aerosol

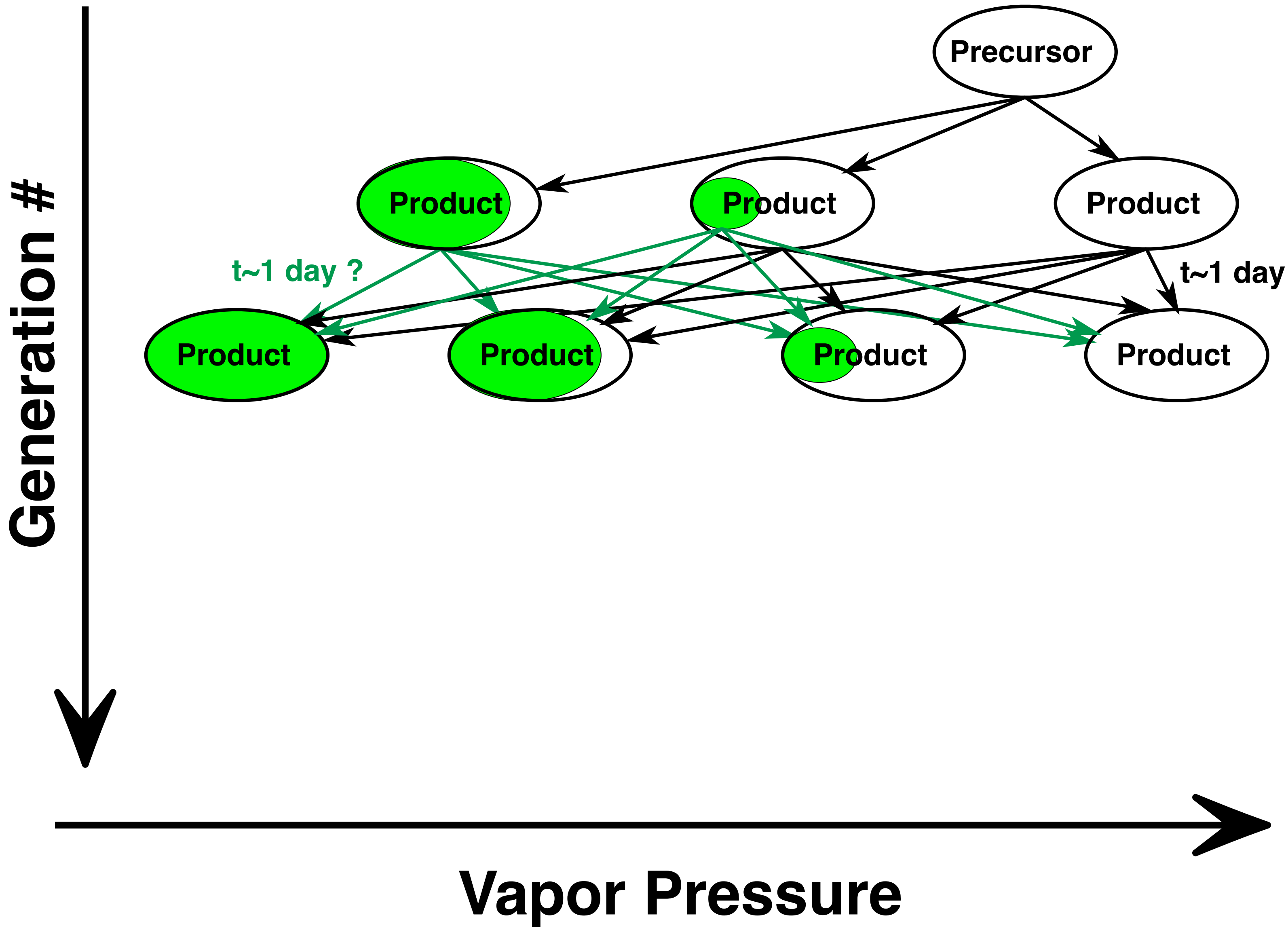


State of the art, in some models...

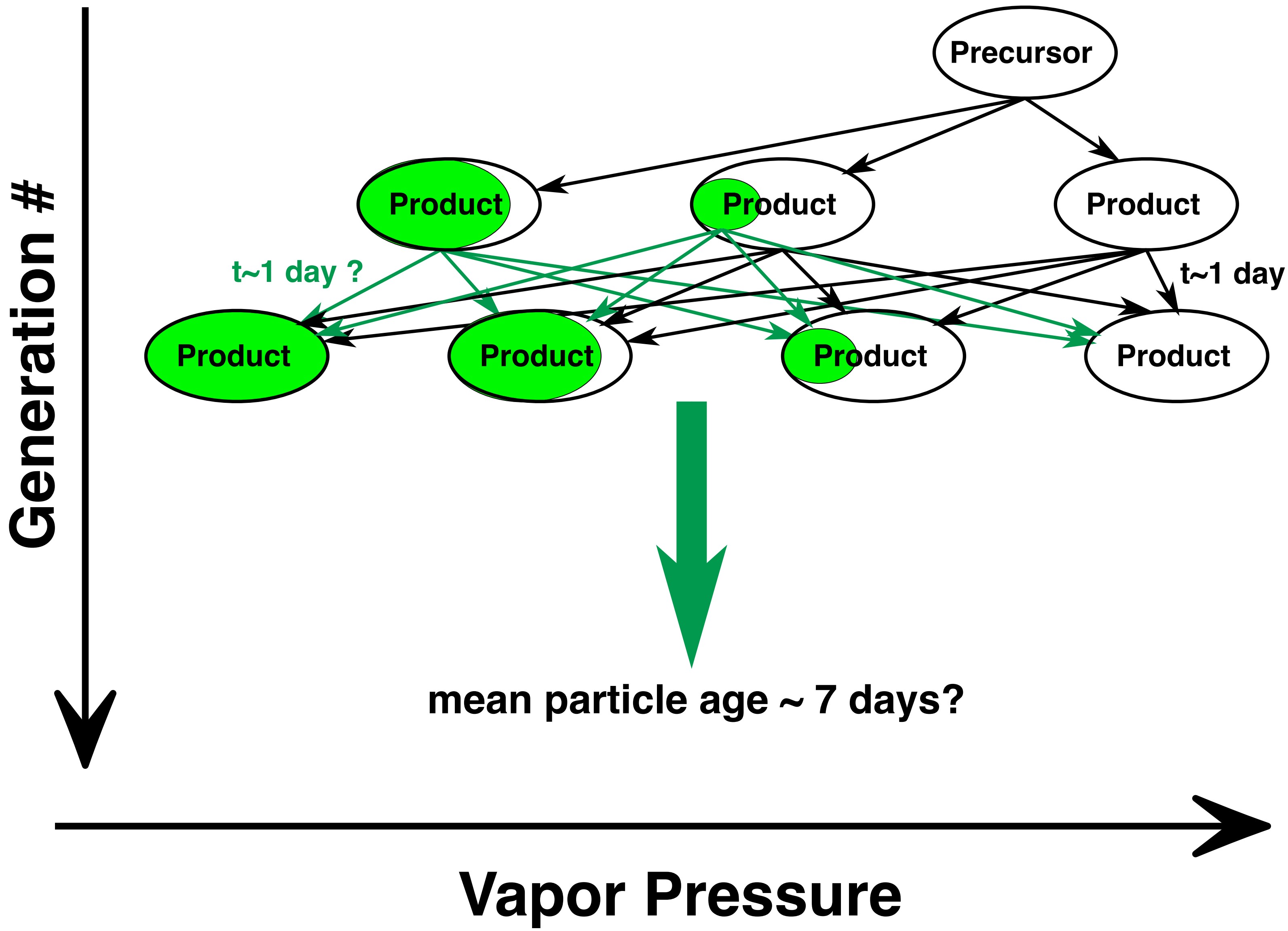
Organic Emissions Processing



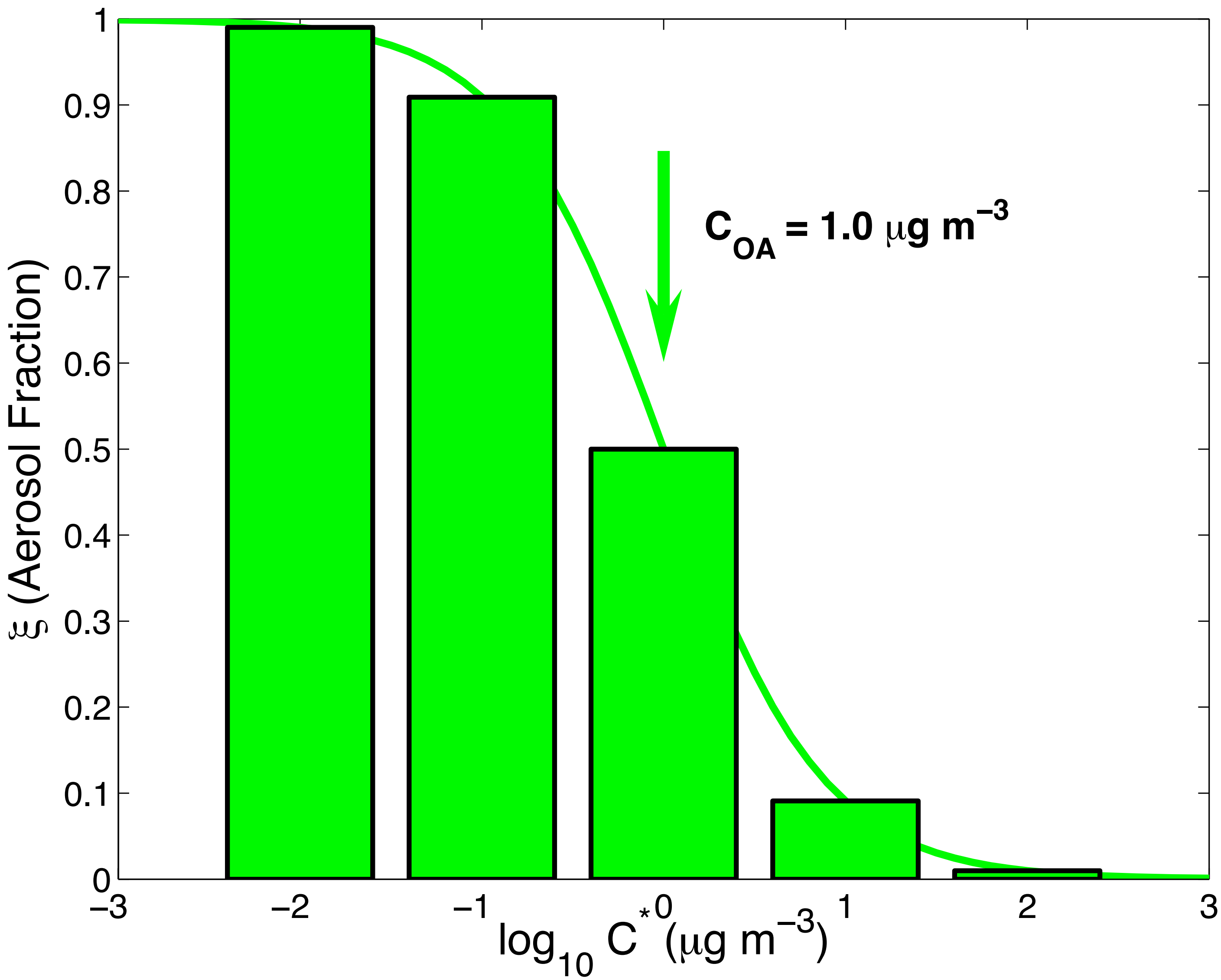
Continued Processing



How Far Does it Go??

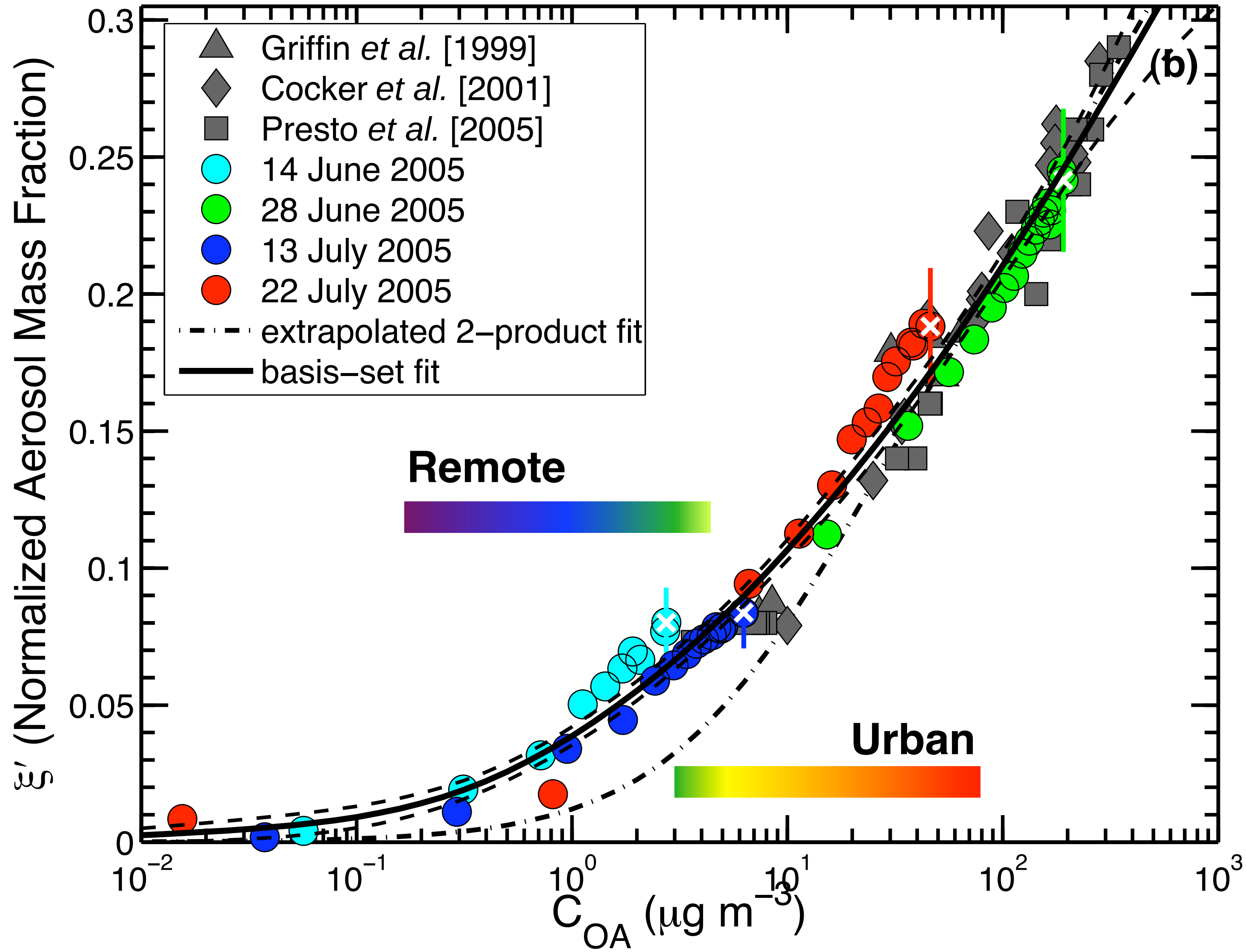


The Volatility Basis Set



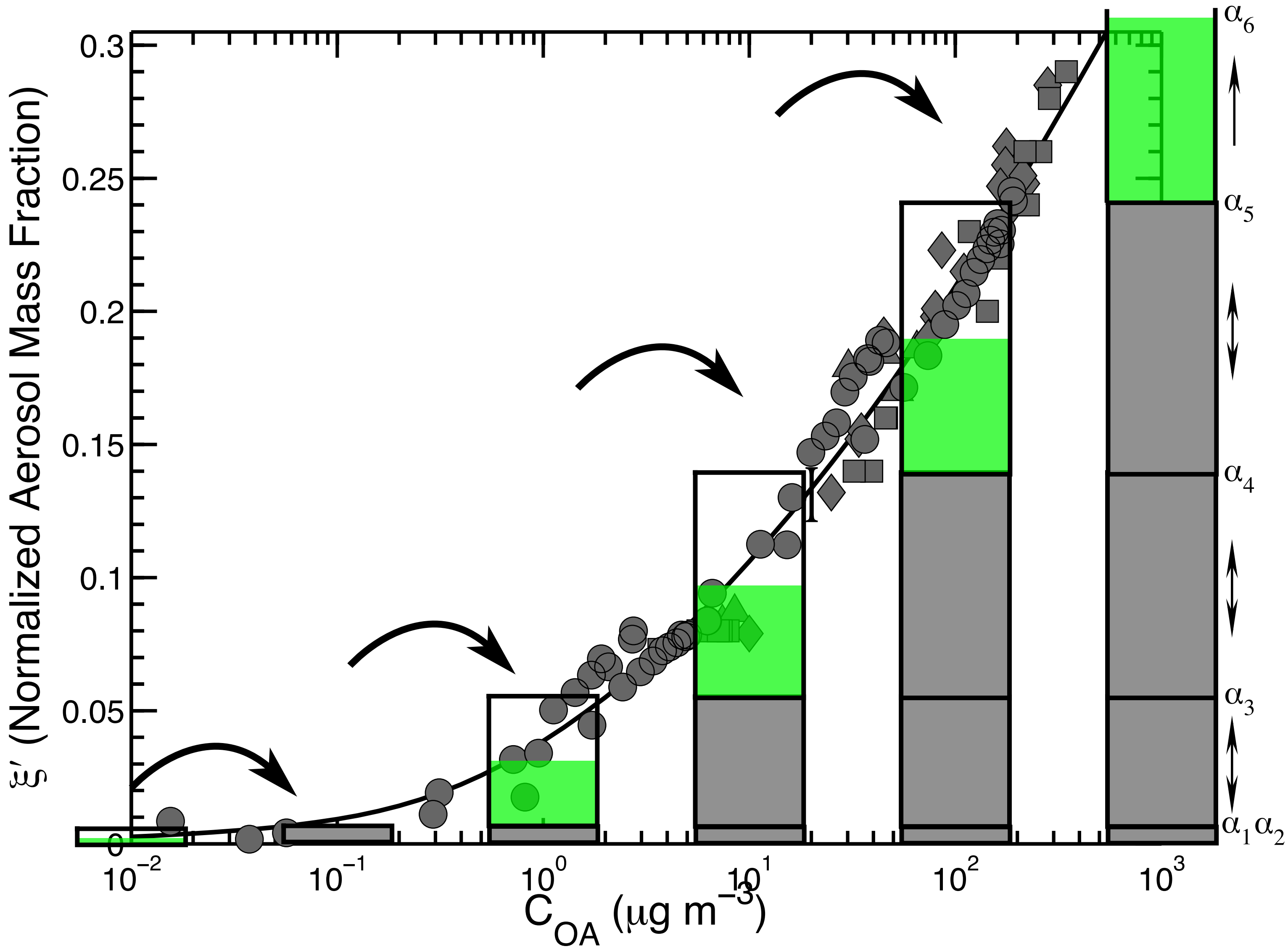
$$C_i^* = \left\{0.01, 0.1, 1, 10, 100, 1000, 10^4, 10^5, 10^6\right\}\ \mu g\, m^{-3}$$

α-pinene + Ozone (low NO_x)



$\sim$ 2x SOA under remote atmospheric conditions vs. extrapolation.

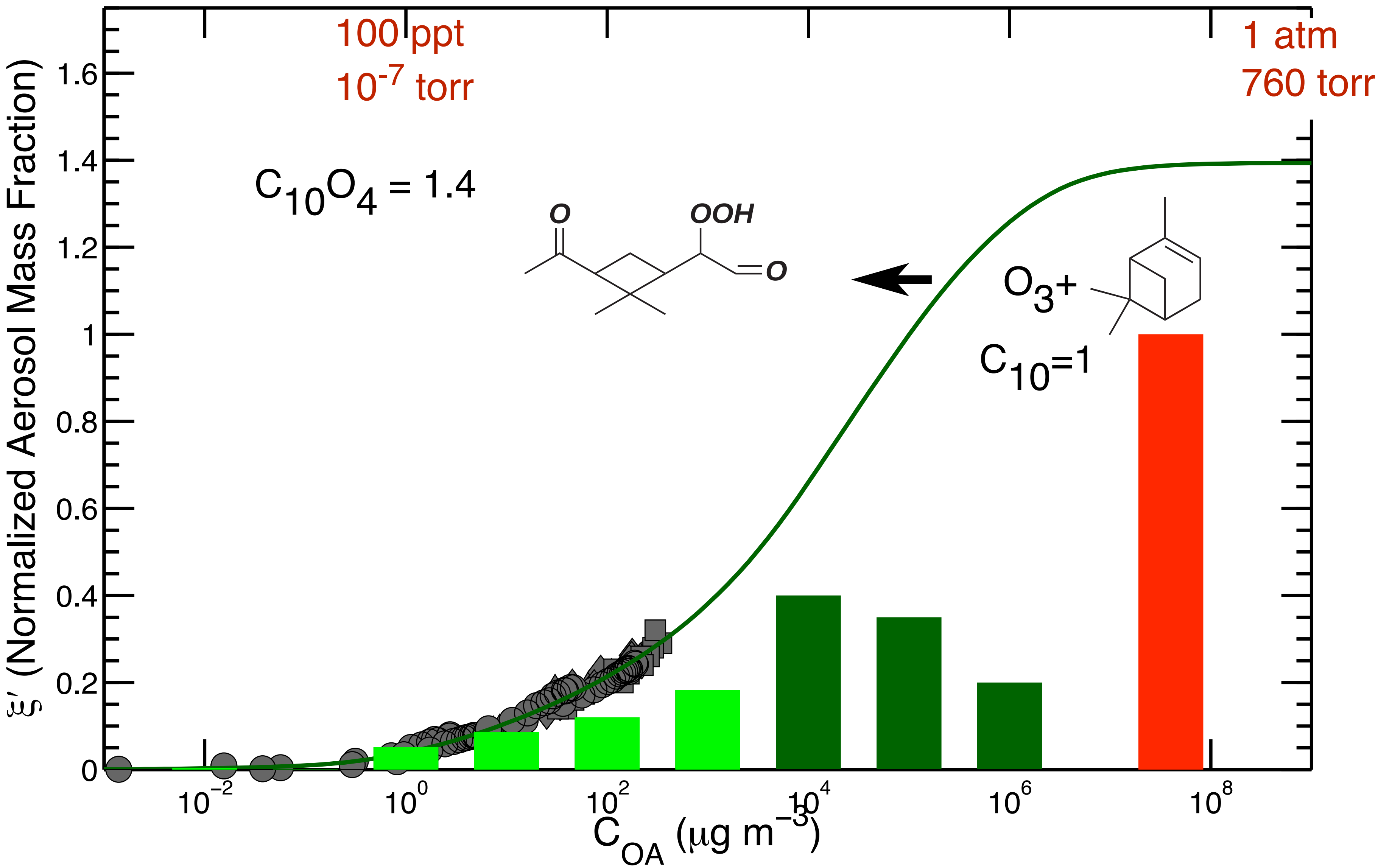
α-pinene and the Basis Set



(mass yields α')

$$\alpha'_{\mathrm{i}} = \{.004, \quad 0, \quad .05, \quad .09, \quad .12, \quad .18, ...\}$$

α-Pinene + Ozone Mass Balance

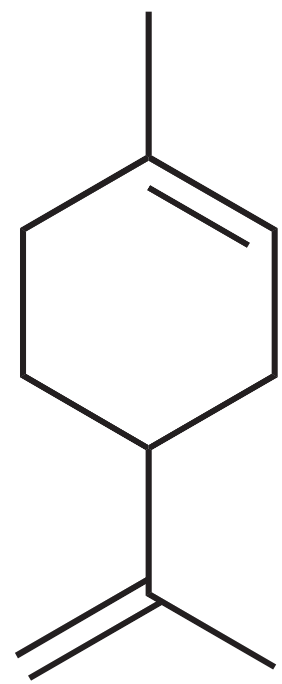


Mass balance for 'nominal product' demands $\xi_{\text{max}} = \sum_i \alpha_i \simeq 1.4$.

Generations in Terpene + O_3

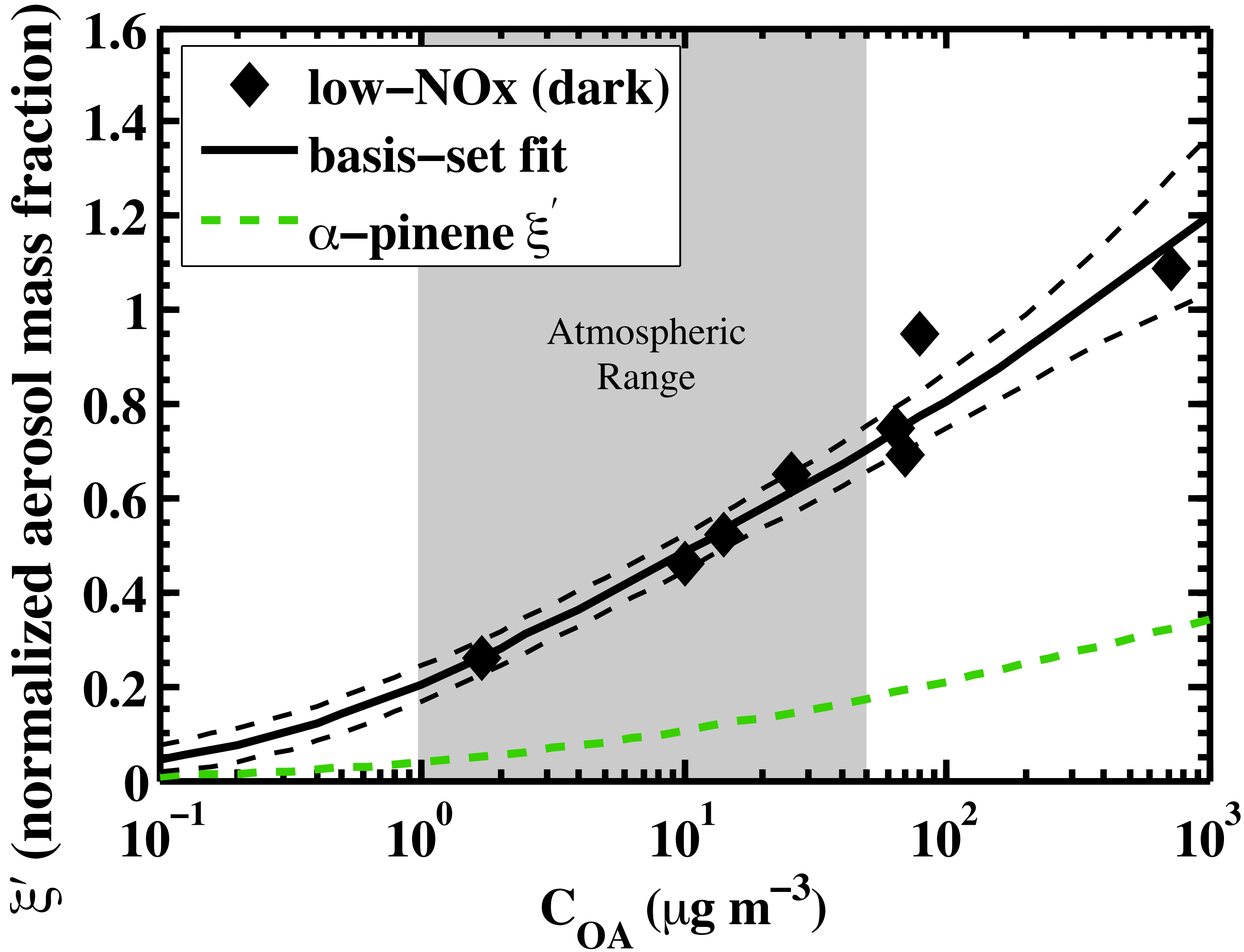
- Multiply unsaturated terpenes like d-limonene should suffer multiple ozonation.
- Which double bond goes first, and what phase is the second reaction in???

$k \simeq 3 \times 10^{-16}$



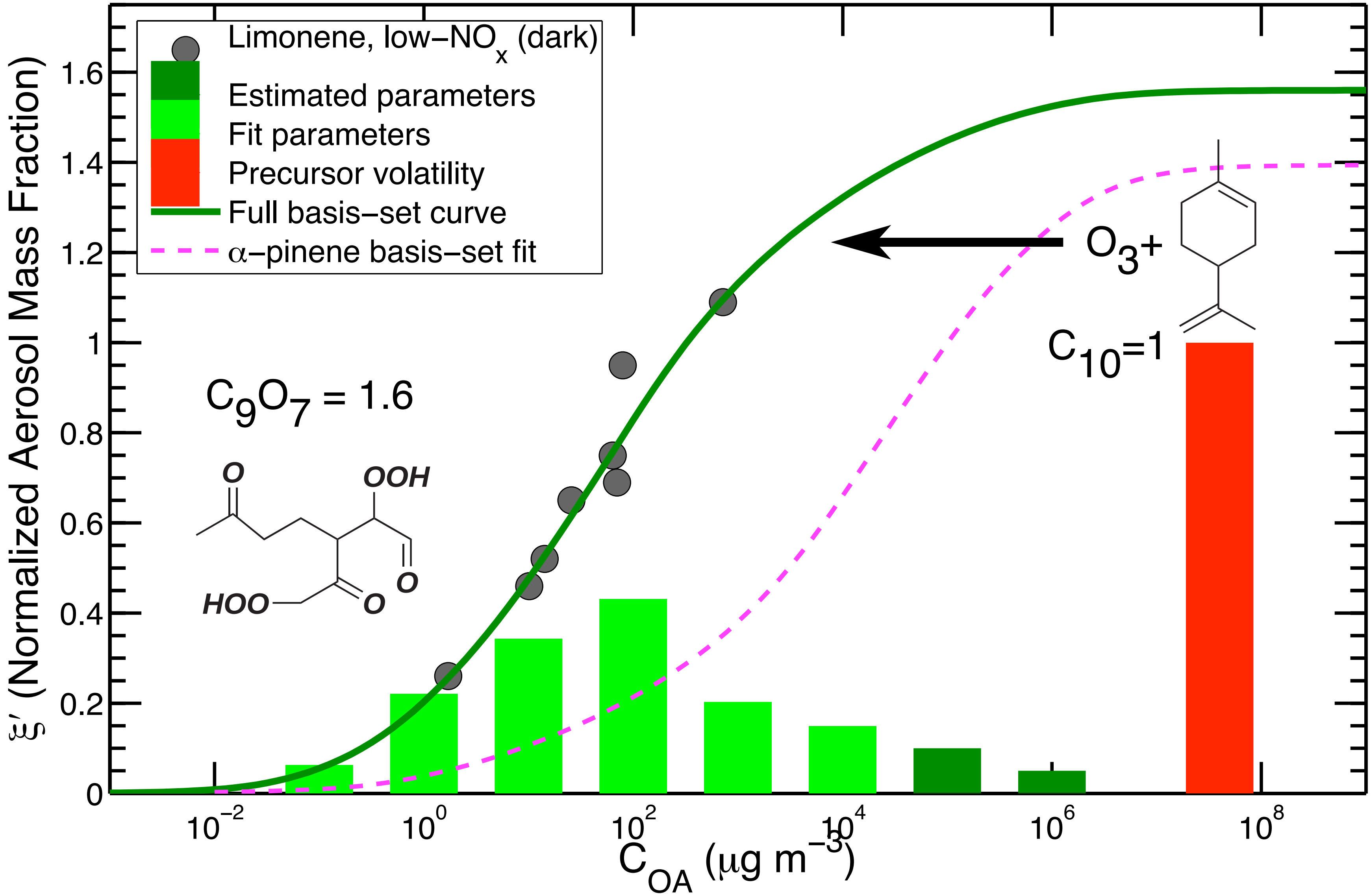
$k \simeq 8 \times 10^{-18}$

Limonene and the Basis Set (1 ppm O_3)



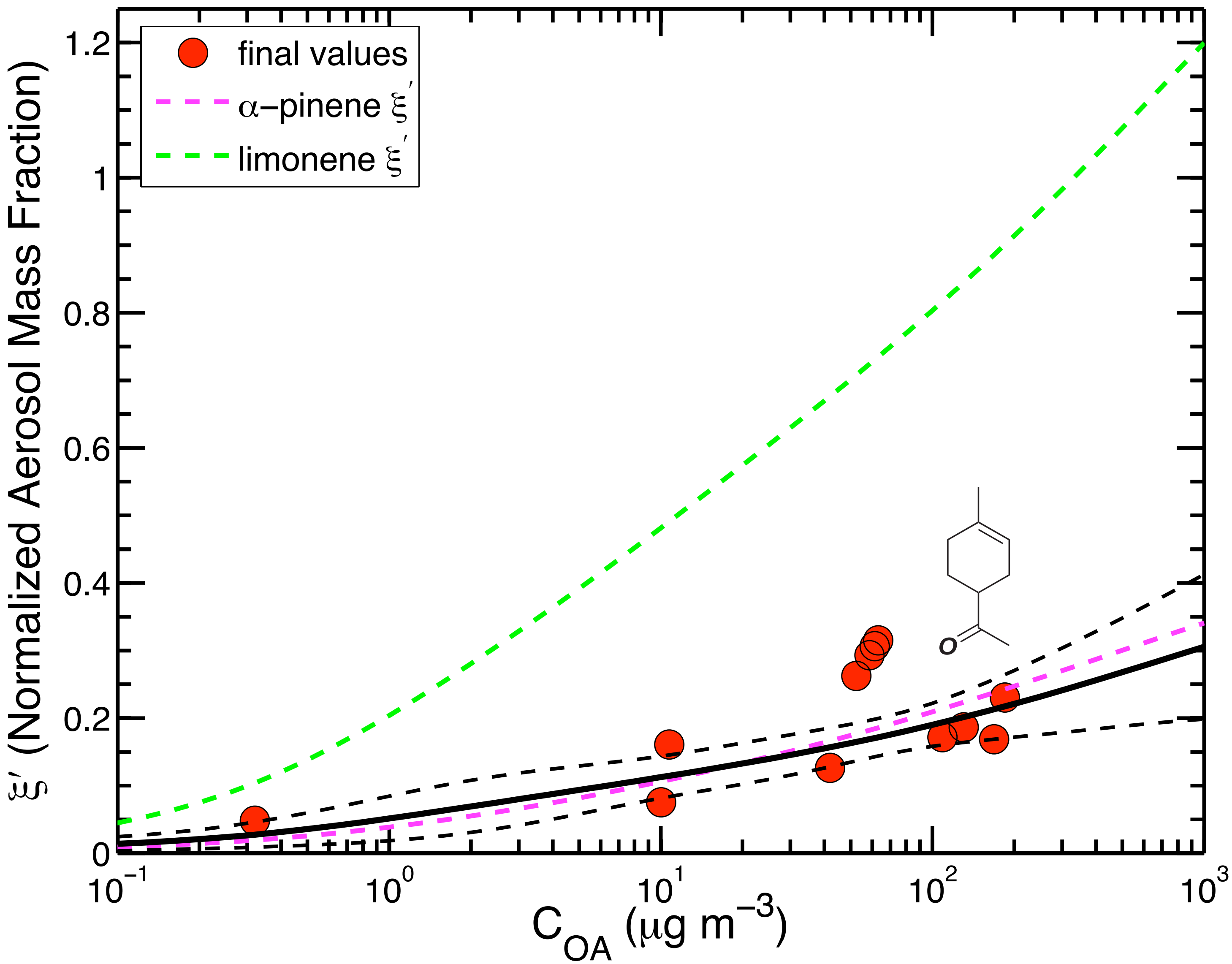
$\alpha'_i = \{.0, \quad .06, \quad .22, \quad .34, \quad .43, \quad .20, \quad .14, \ldots\}$

Limonene + Ozone Mass Balance



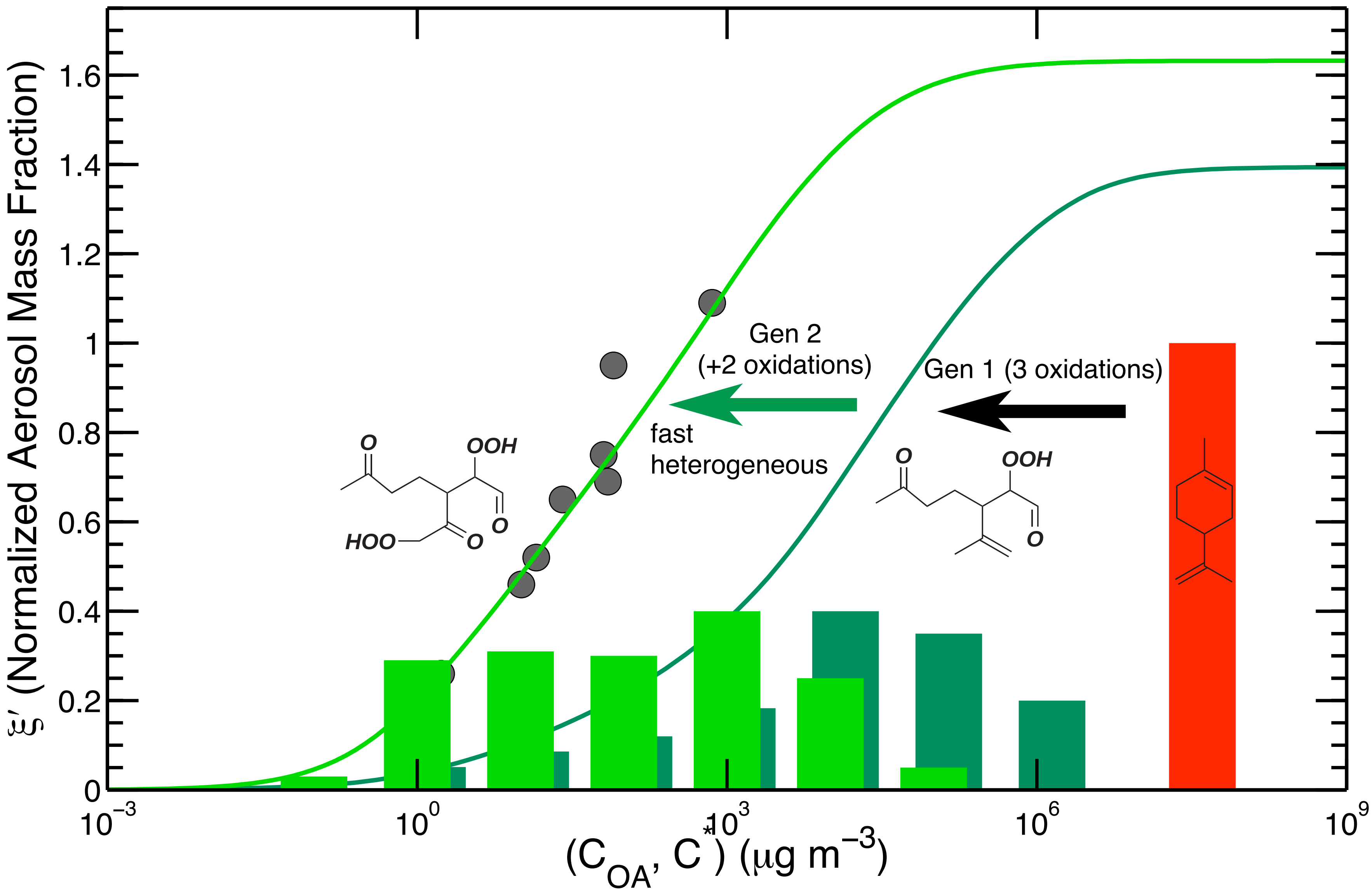
D-limonene + O_3 makes more SOA than α-pinene.

Limonaketone + Ozone



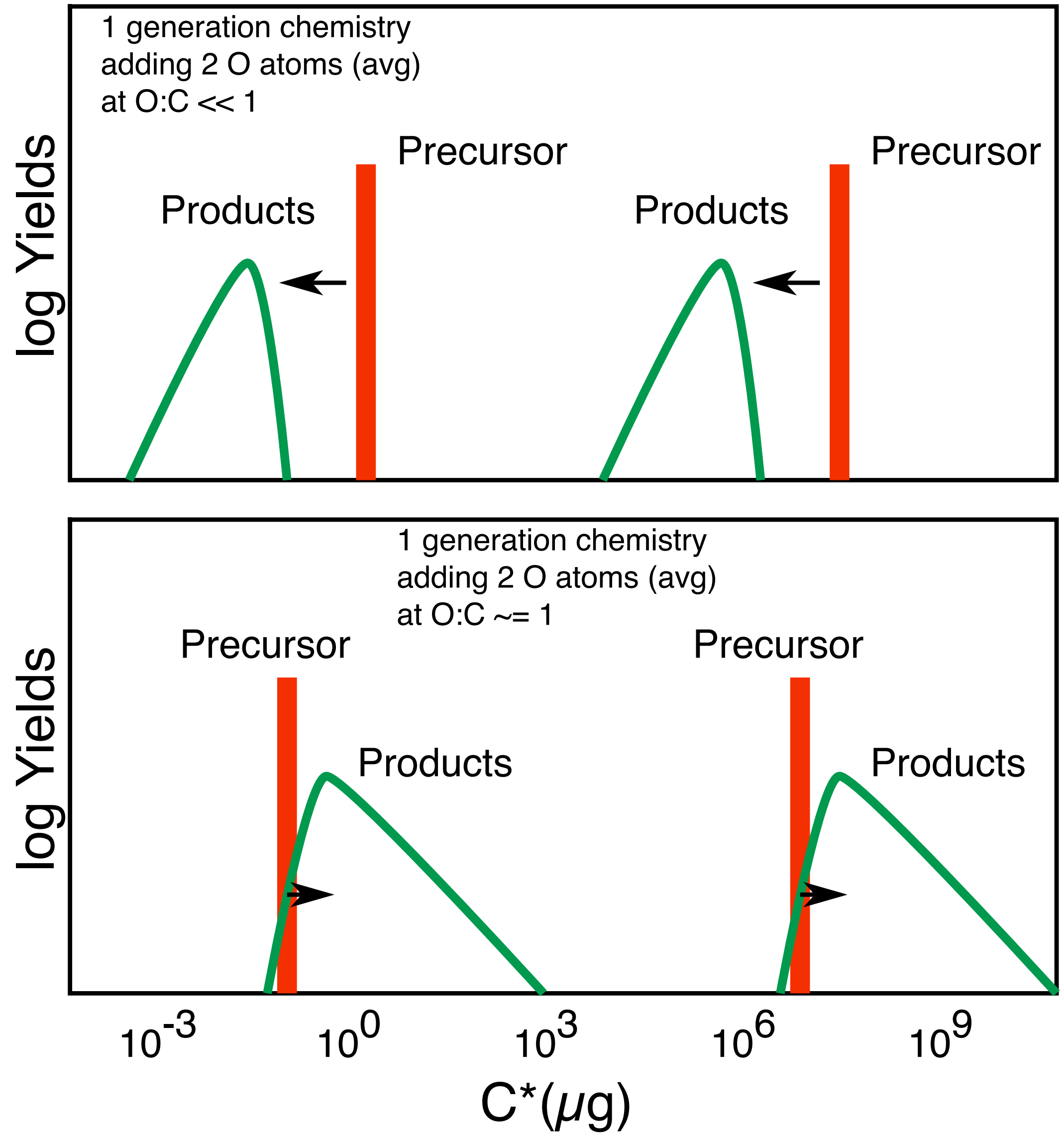
But limonoketone is just like α-pinene.

Generations of Limonene Oxidation



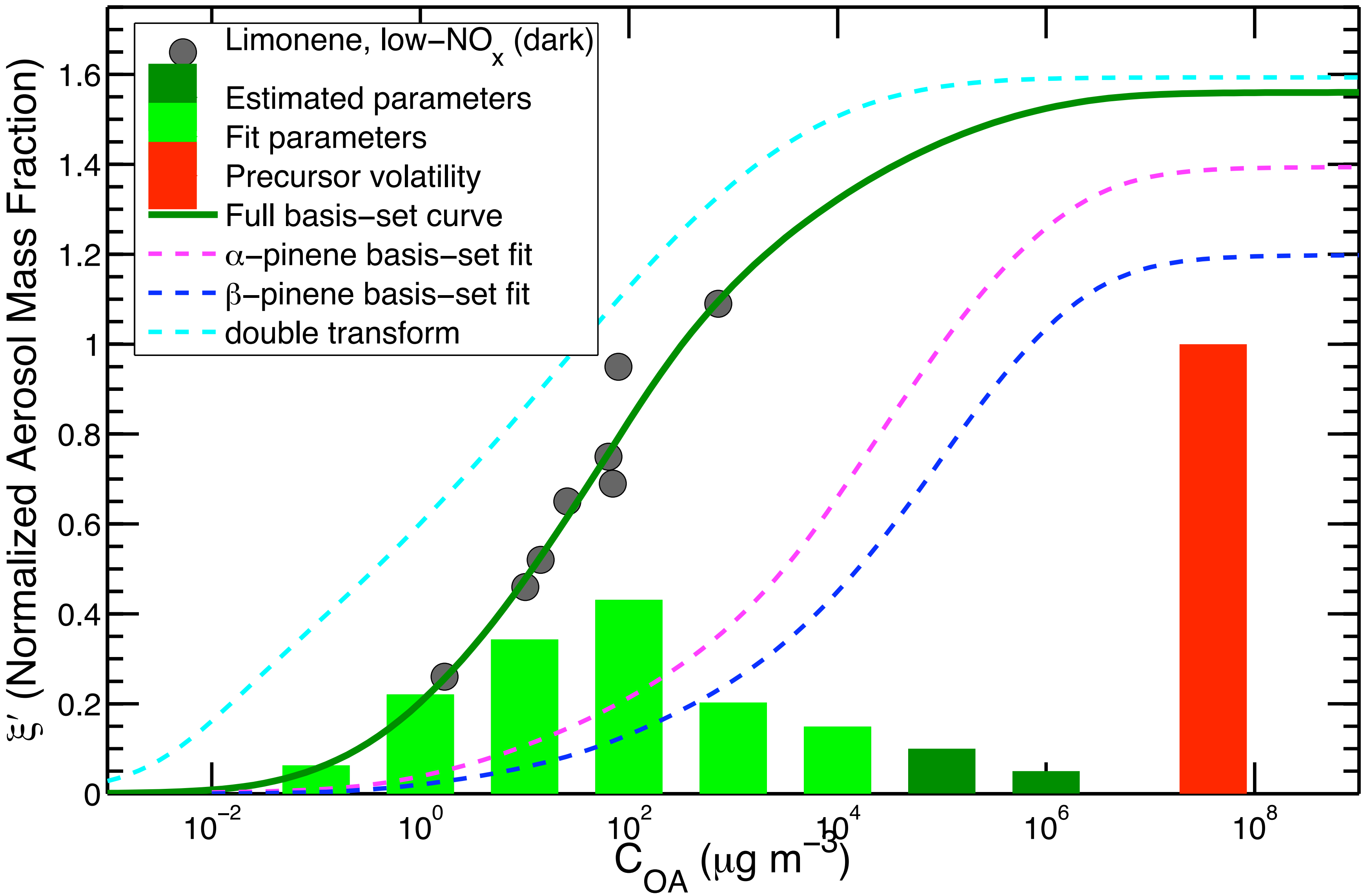
What happens with 2nd oxidation on real aerosol??.

Operators in C* Space



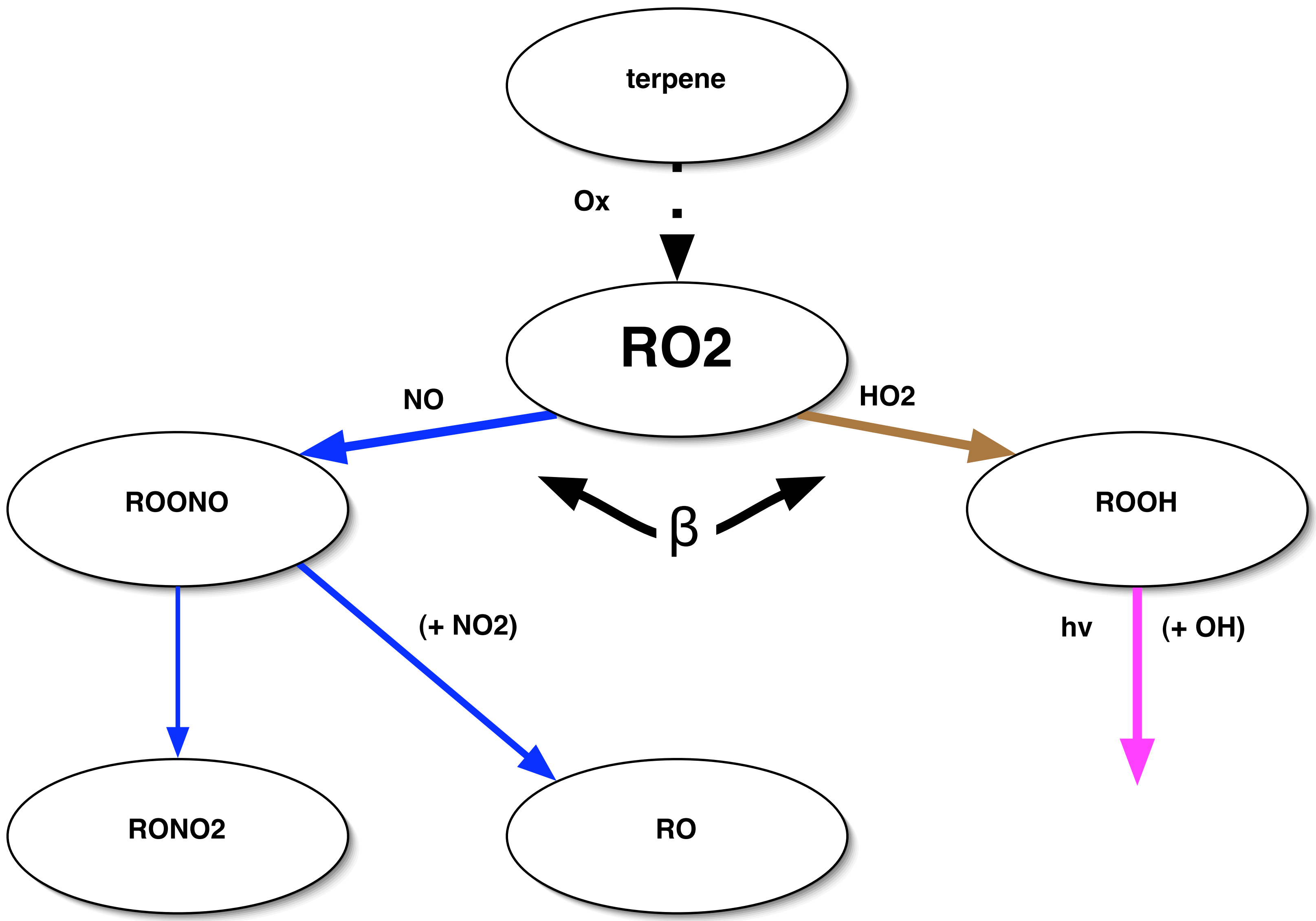
Ox at low O:C lowers C*; Ox at O:C $\simeq$ 1 raises C* b/c C-C bonds break.

Limonene Operator Test

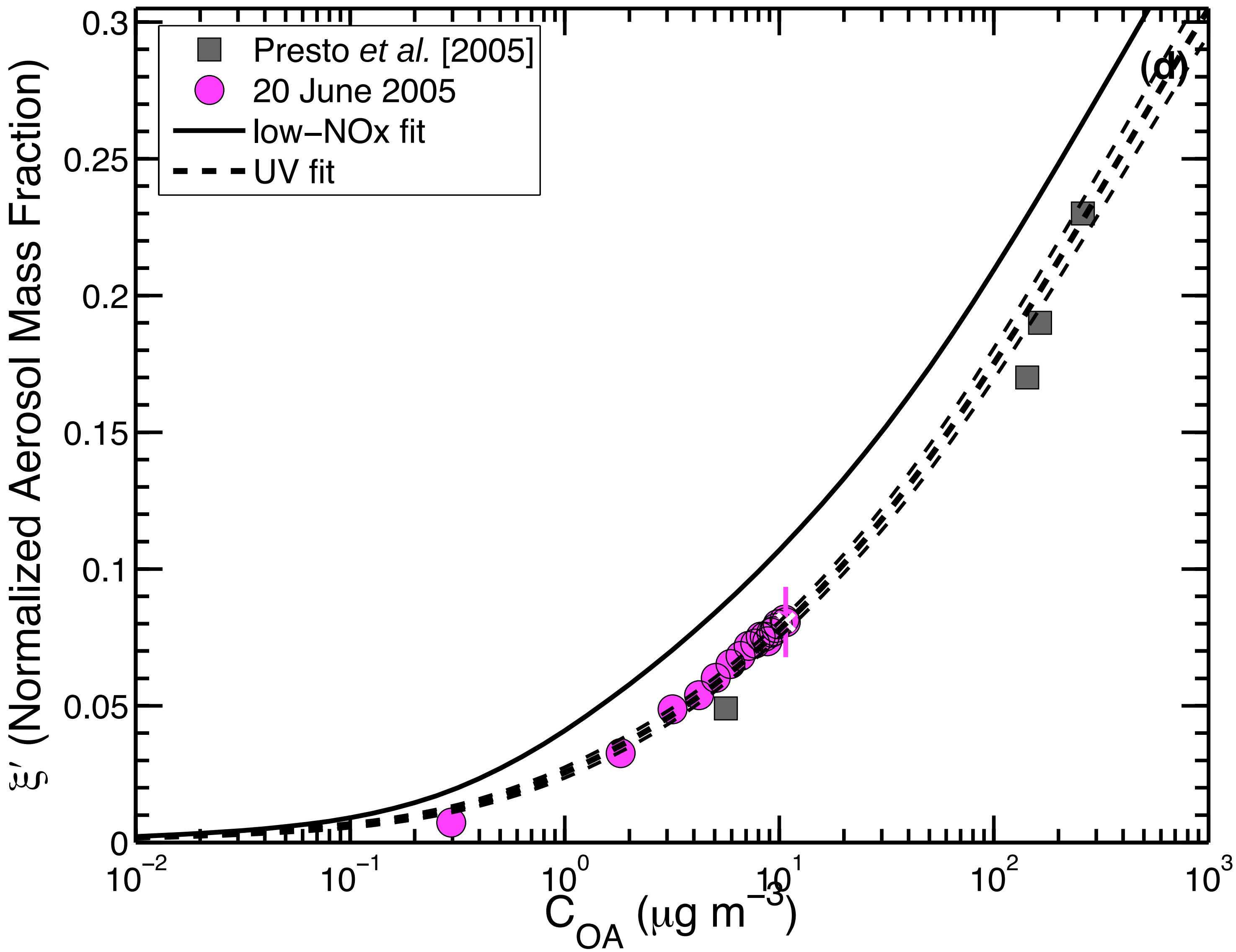


Limonene products actually seem to be somewhat more volatile than we would expect.

RO_2 Fate



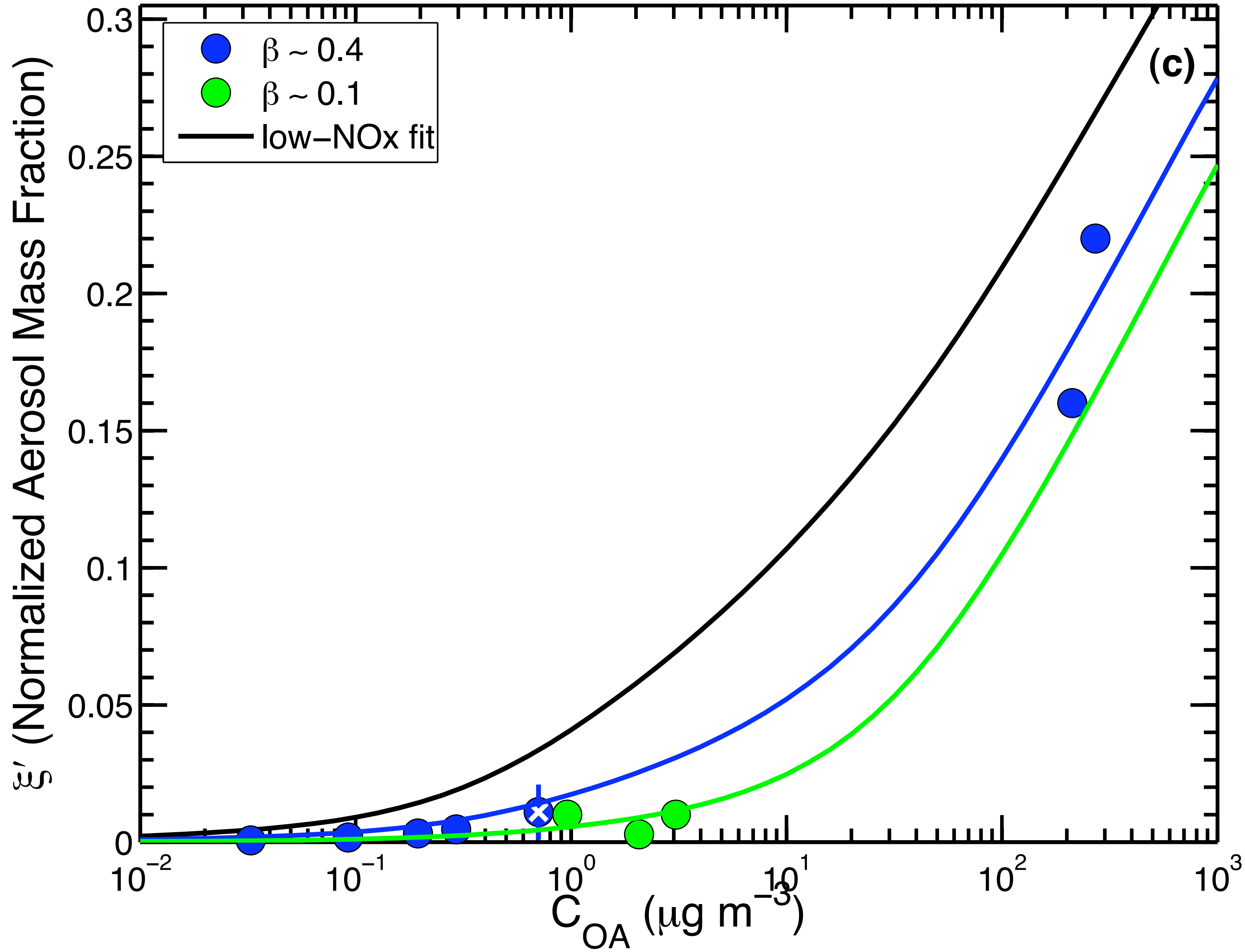
α-pinene + Ozone: UV (no NO_x)



$$\alpha'_i = \{.004, \quad 0, \quad .05, \quad .09, \quad .12, \quad .18, ...\}$$

$\downarrow$ UV

$$\alpha'_i(\mathrm{UV}) = \{.004, \quad 0, \quad .02, \quad .08, \quad .12, \quad .18, ...\}$$

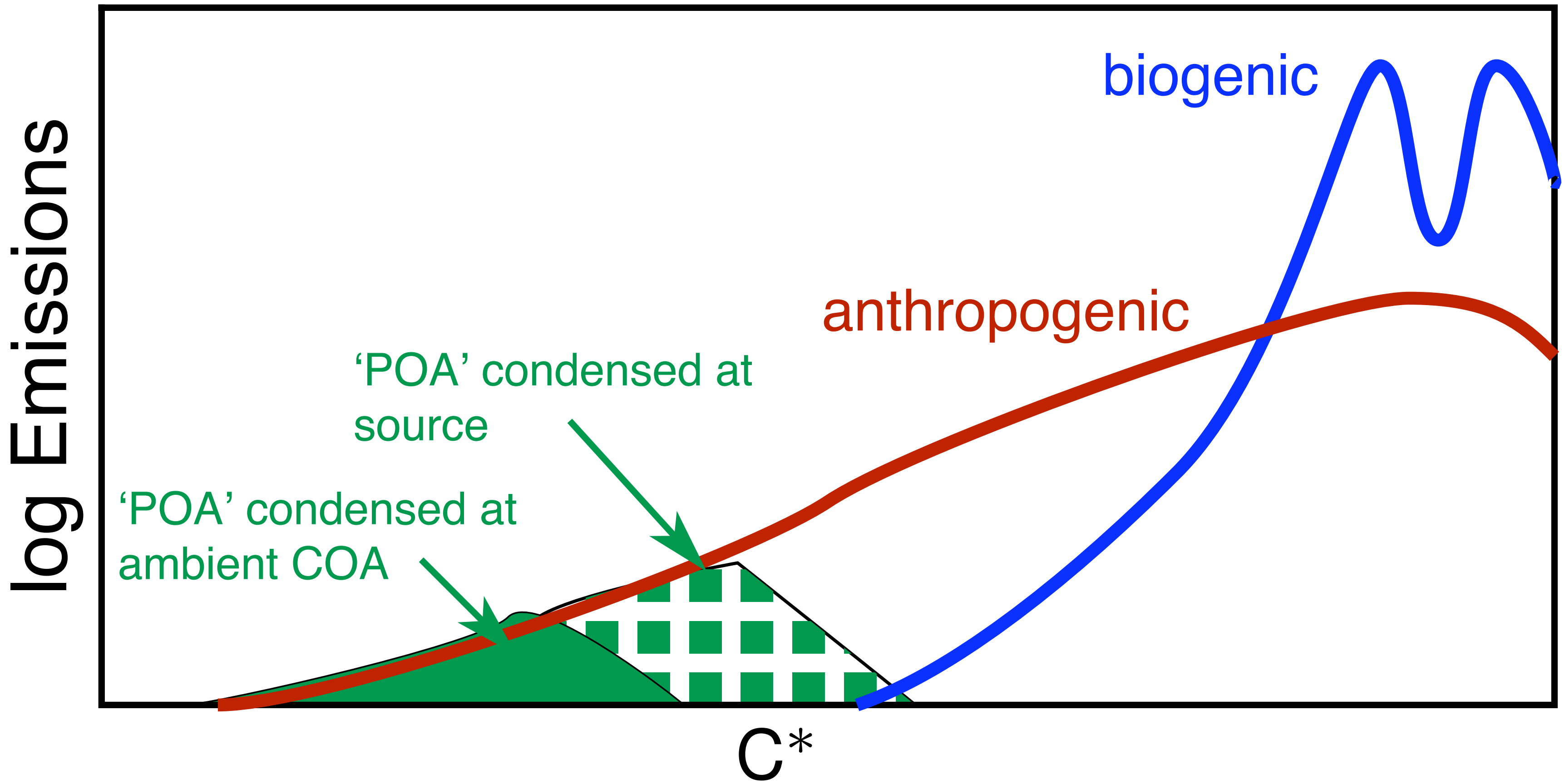


$$\alpha_i'(HO_2) \quad = \quad \{.004, \quad 0, \quad .05, \quad .09, \quad .12, \quad .18, \ldots\}$$

$$\downarrow NO_x \quad \beta = (VOC : NO_x)_0/10, (VOC : NO_x)_0 < 10$$

$$\alpha_i'(NO_x) \quad = \quad \{0, \quad 0, \quad 0, \quad 0, \quad .15, \quad .2, \ldots\}$$

The Big Picture



Conclusions