UNIVERSITY OF EASTERN FINLAND

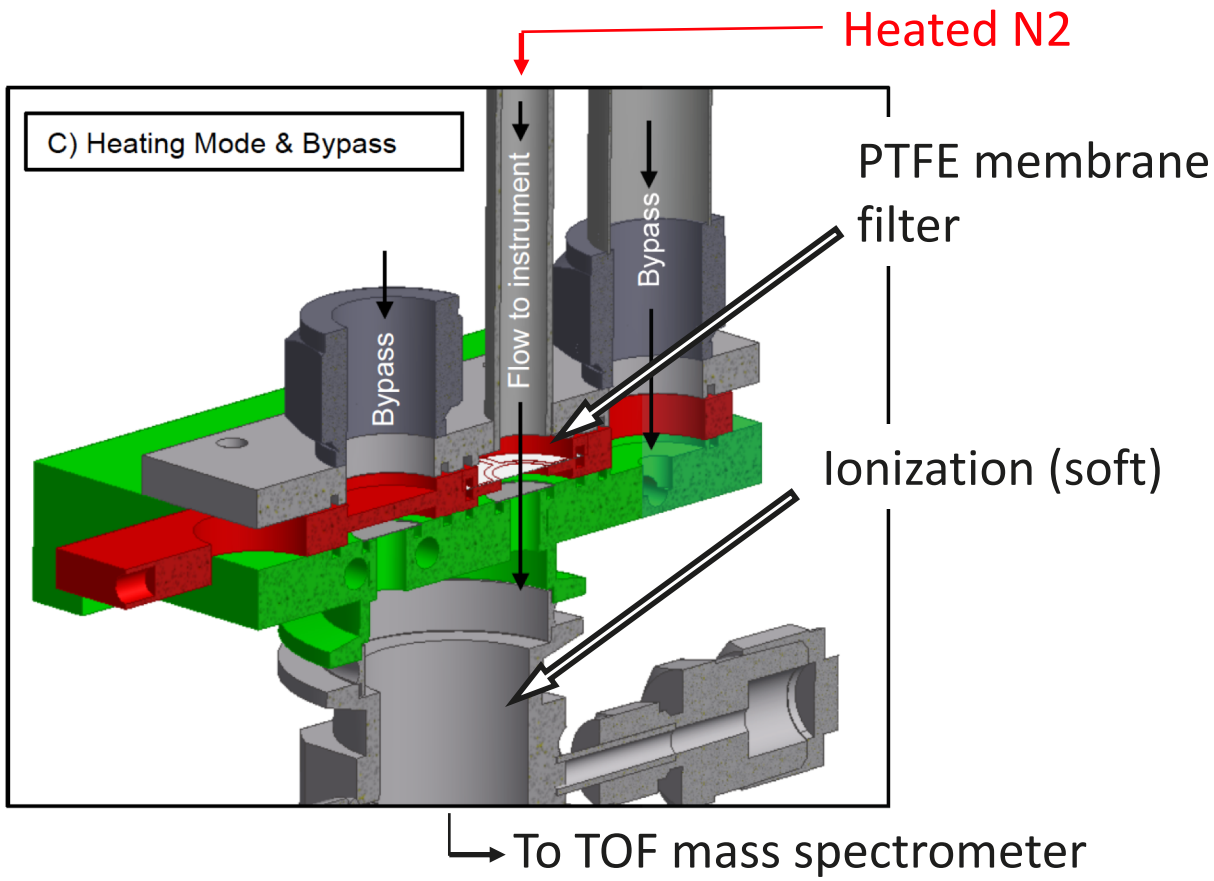
Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

International Aerosol Modeling Algorithms Conference
Davis, Dec. 4-6, 2019

Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

Filter Inlet for Gas and AEROsol (FIGAERO)

Lopez-Hilfiker et al., AMT, 2014



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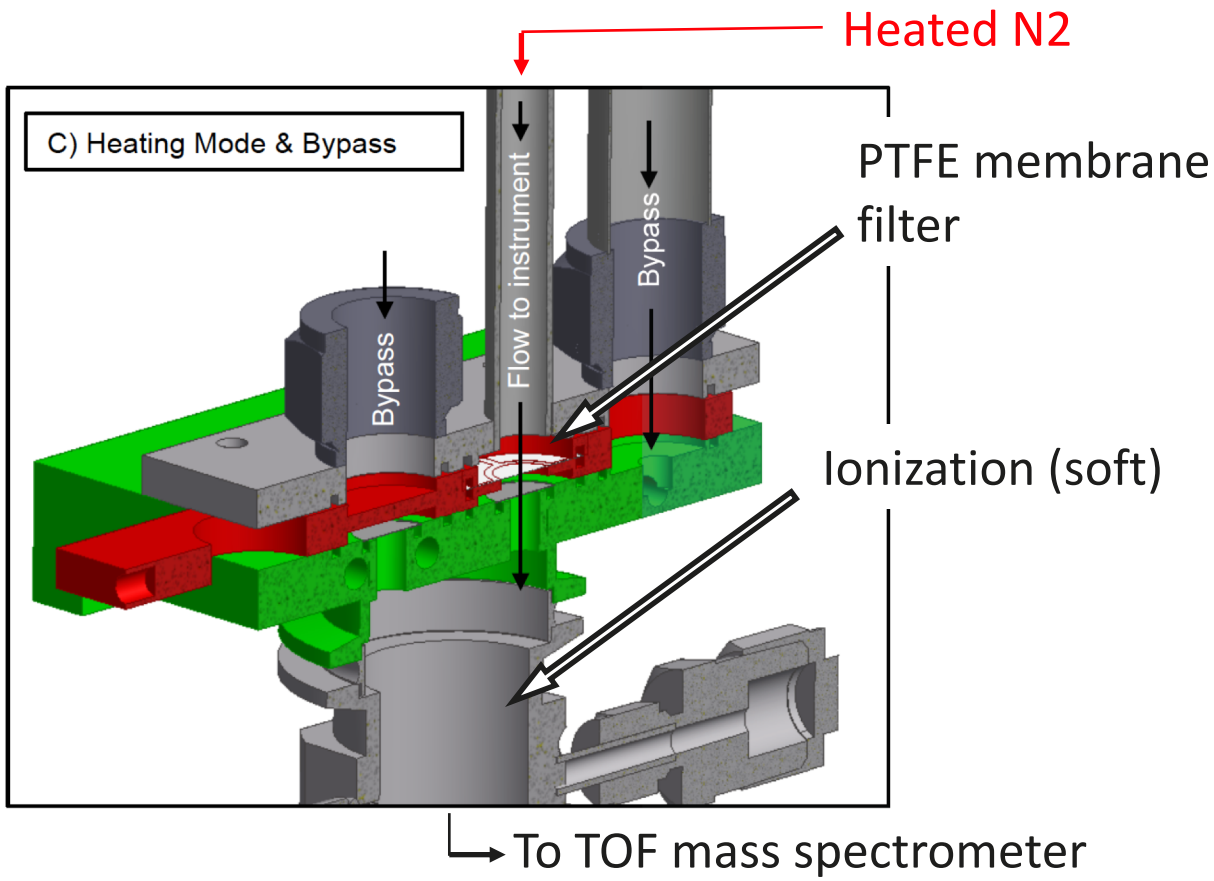

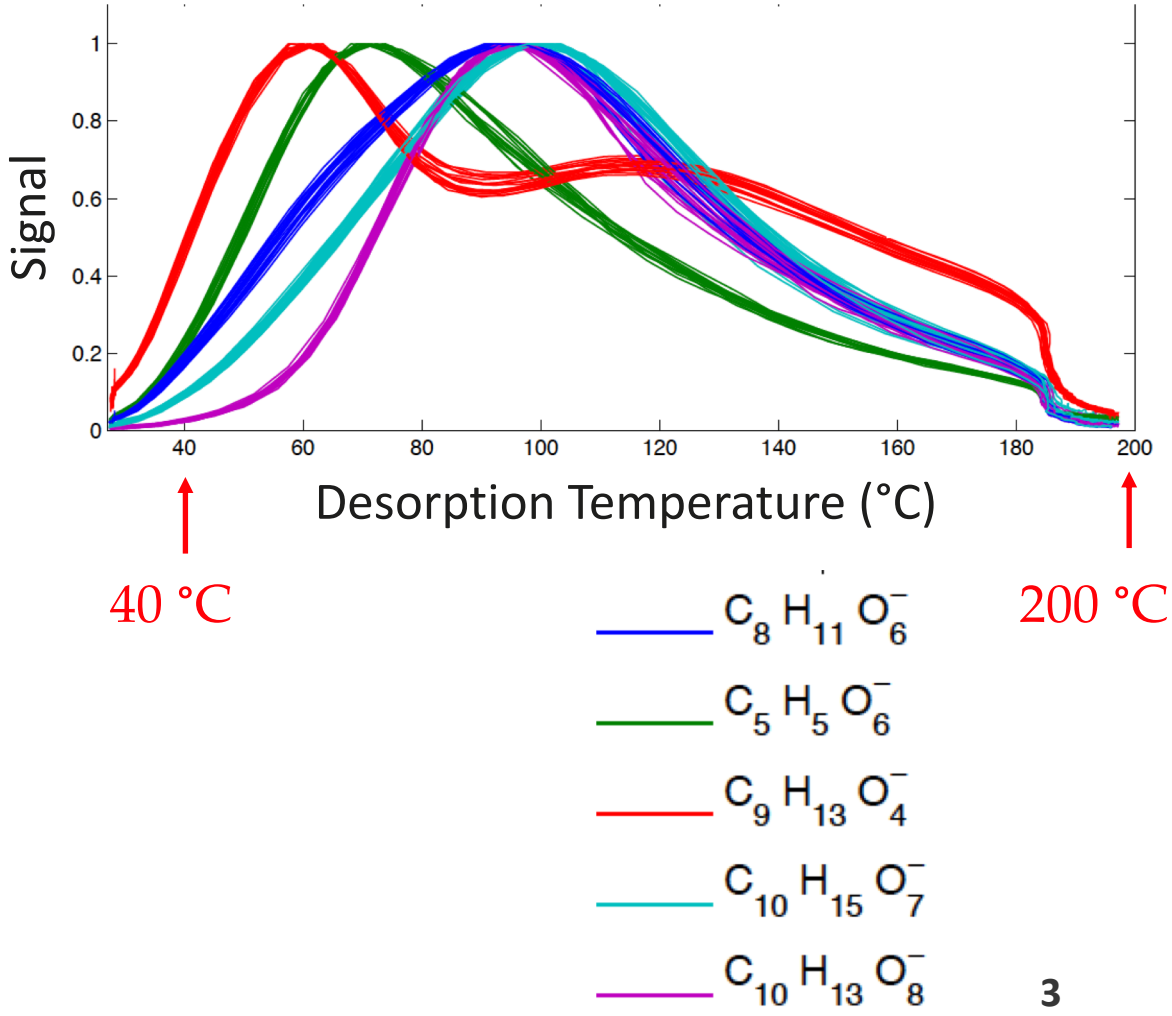

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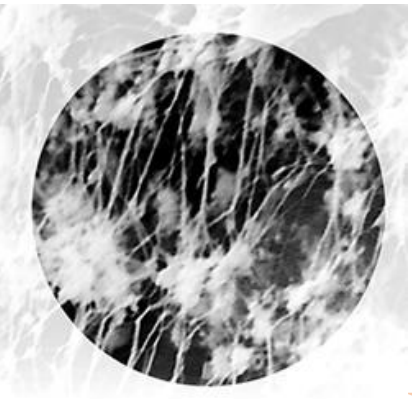
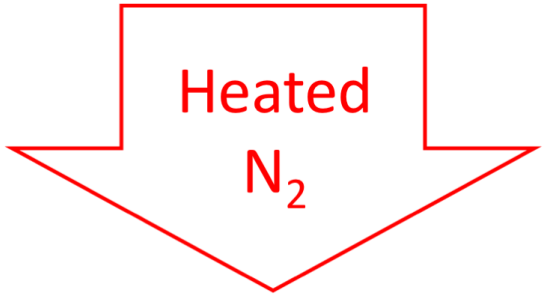
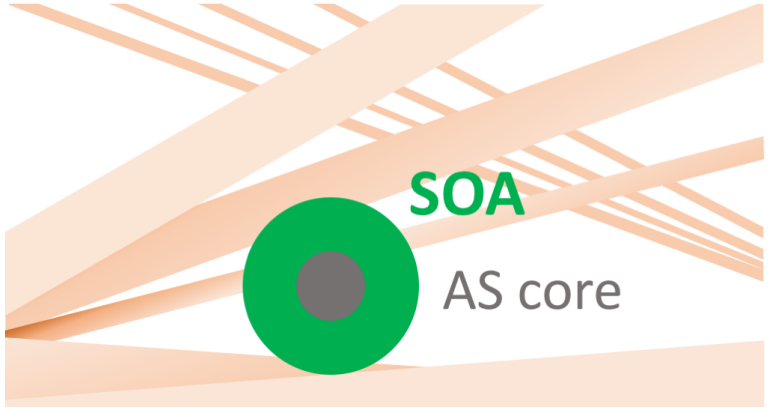
Schobesberger et al., Atmos. Chem. Phys., 2018 (doi: 10.5194/acp-18-14757-2018)

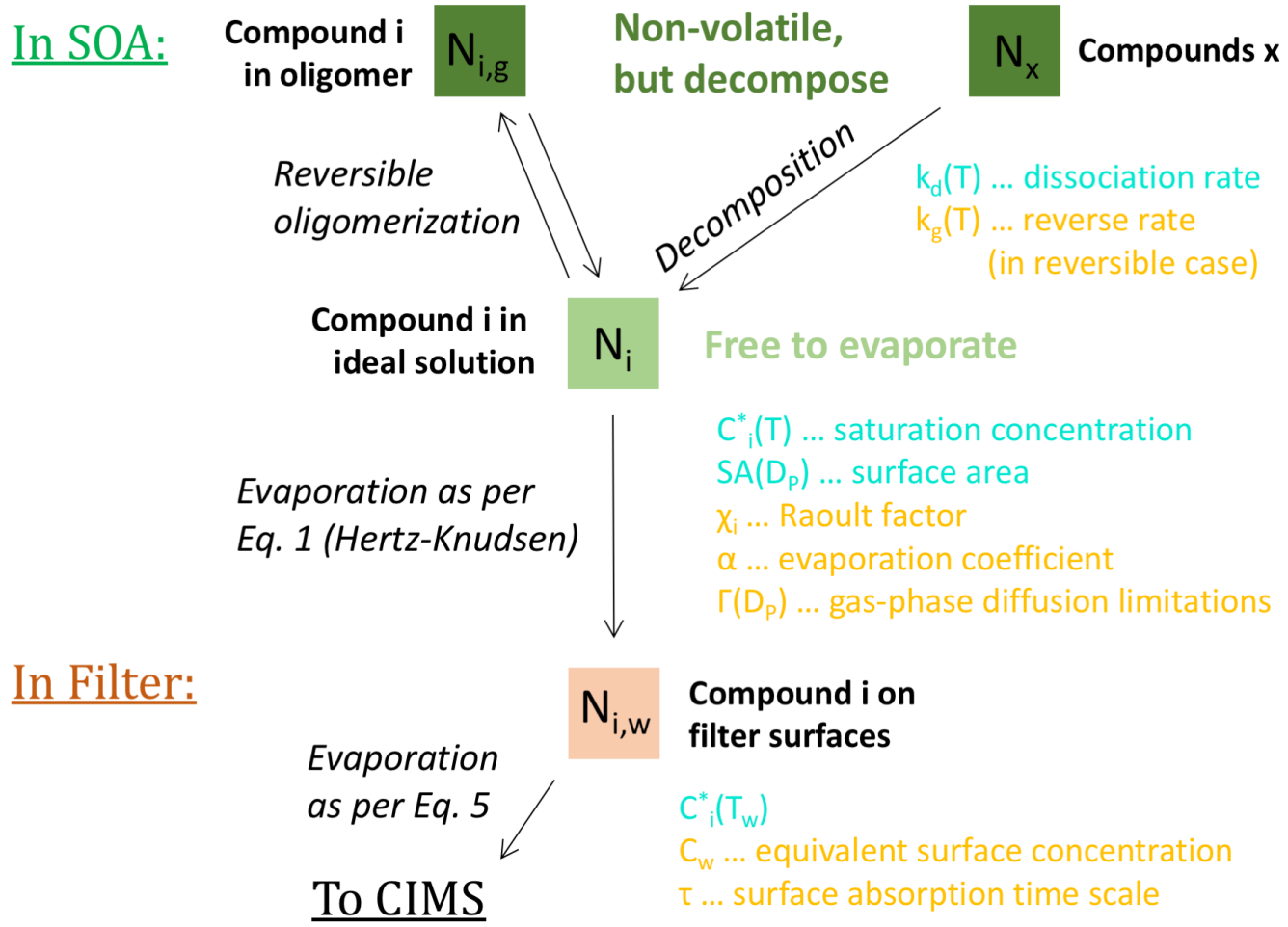


Zefluor® (Pall):
PTFE membrane,
2 µm pore size



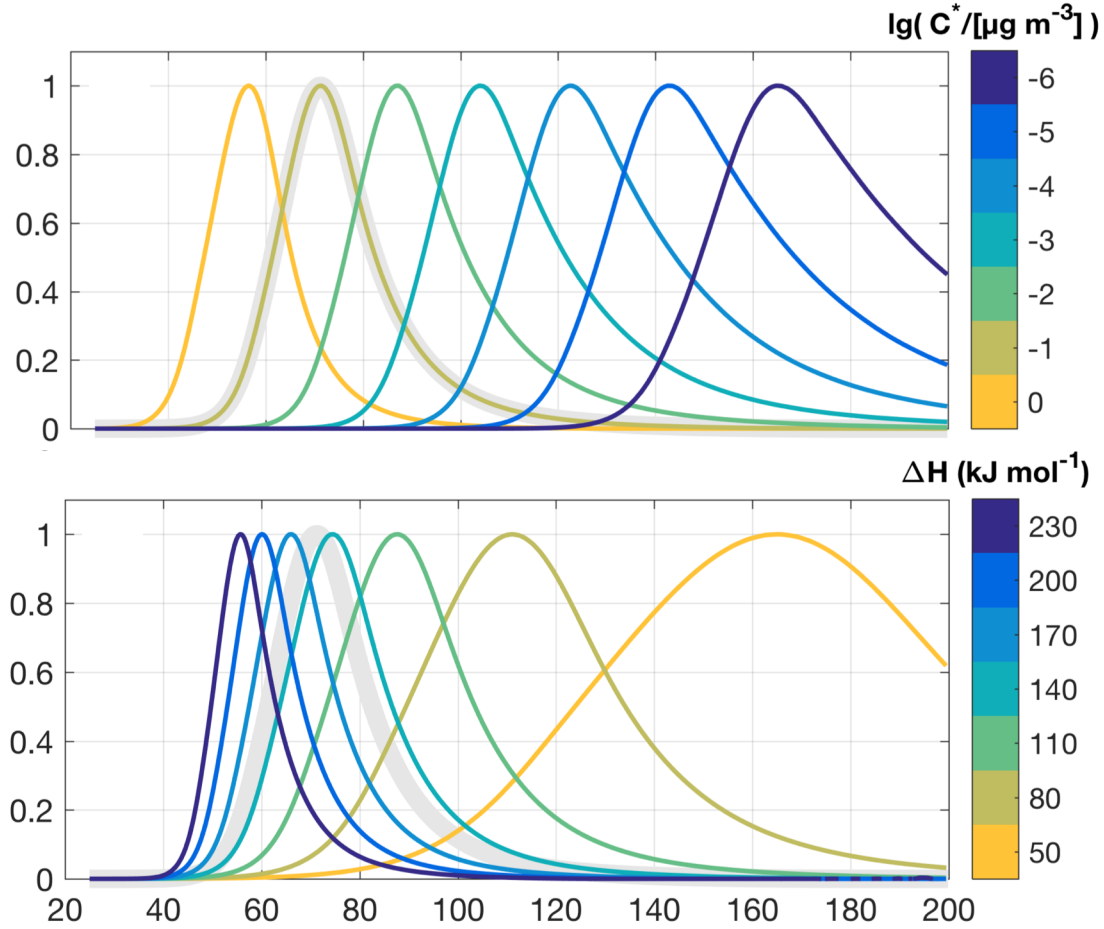
Filter:
PTFE micro-web/membrane





Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

Peak position in principle a function of vapor pressure (~C^*) and vaporization enthalpy (ΔH)



~vapor pressure at room temperature

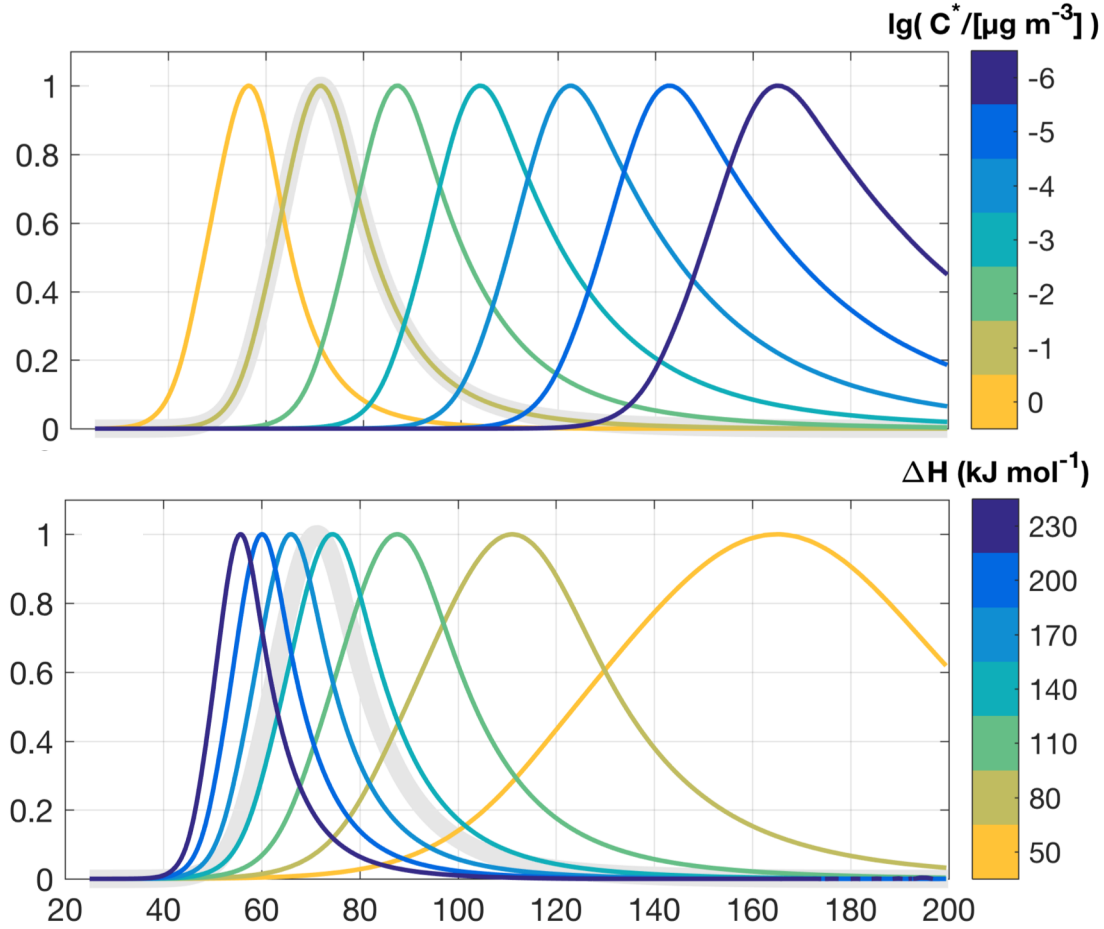
enthalpy of vaporization

$$k_{des} = f \cdot C^*_{i,0} \cdot e^{-\frac{\Delta H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}$$

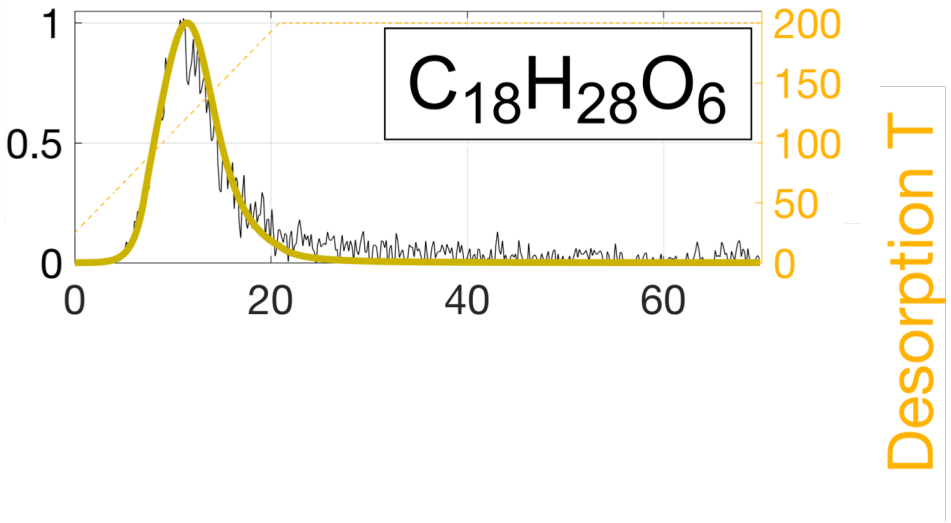
factor (< 1) to account for vapor-surface interactions, in particular PTFE filter (assumed constant here)

Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

Peak position in principle a function of vapor pressure (~C^*) and vaporization enthalpy (ΔH)



E.g.:



0.25	60
C^* (µg m^{-3})	ΔH (kJ mol^{-1})

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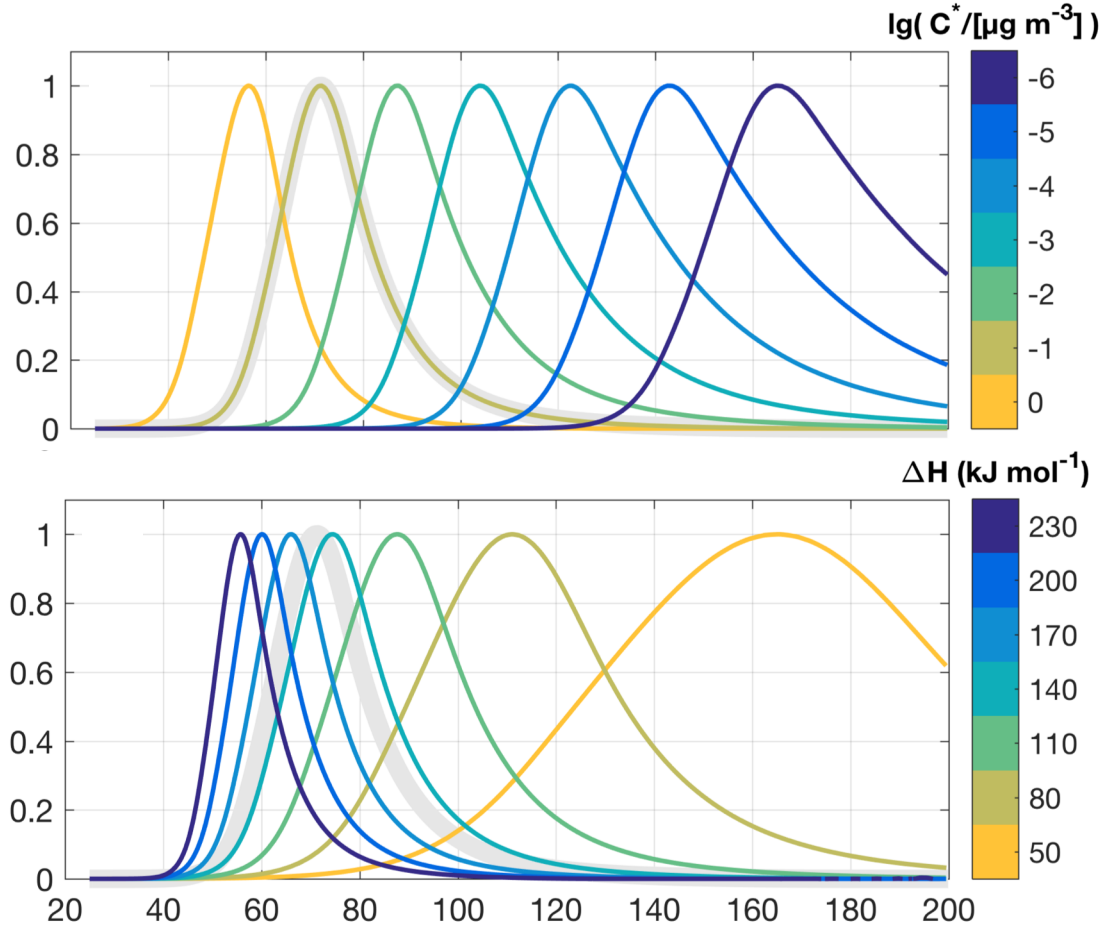

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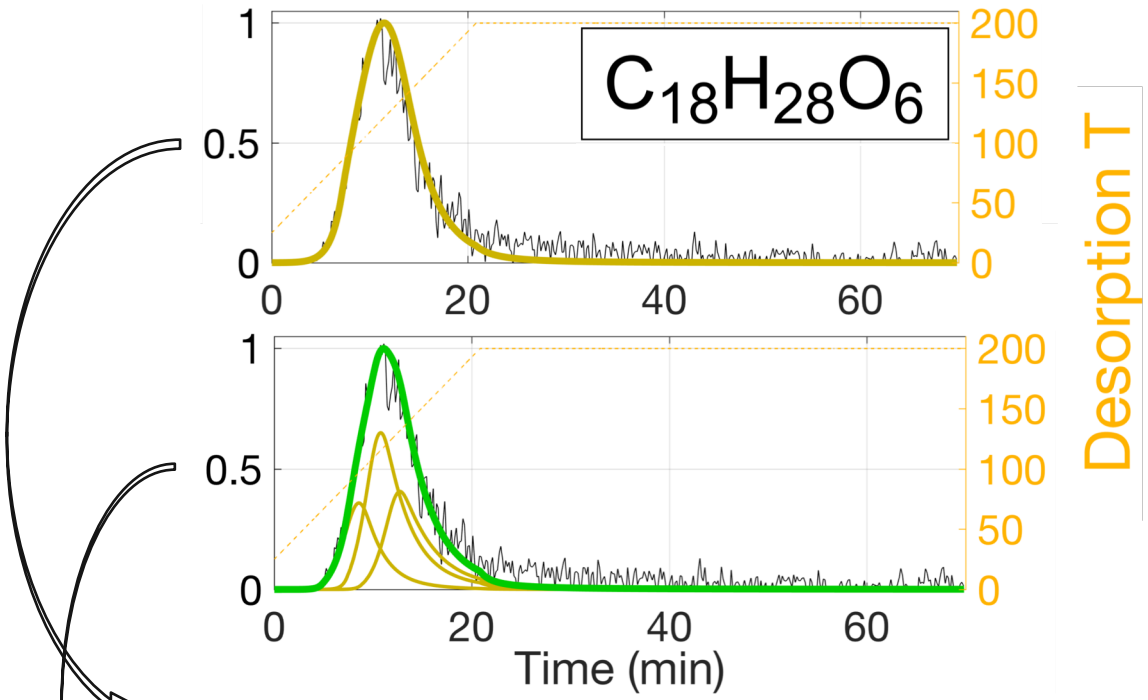
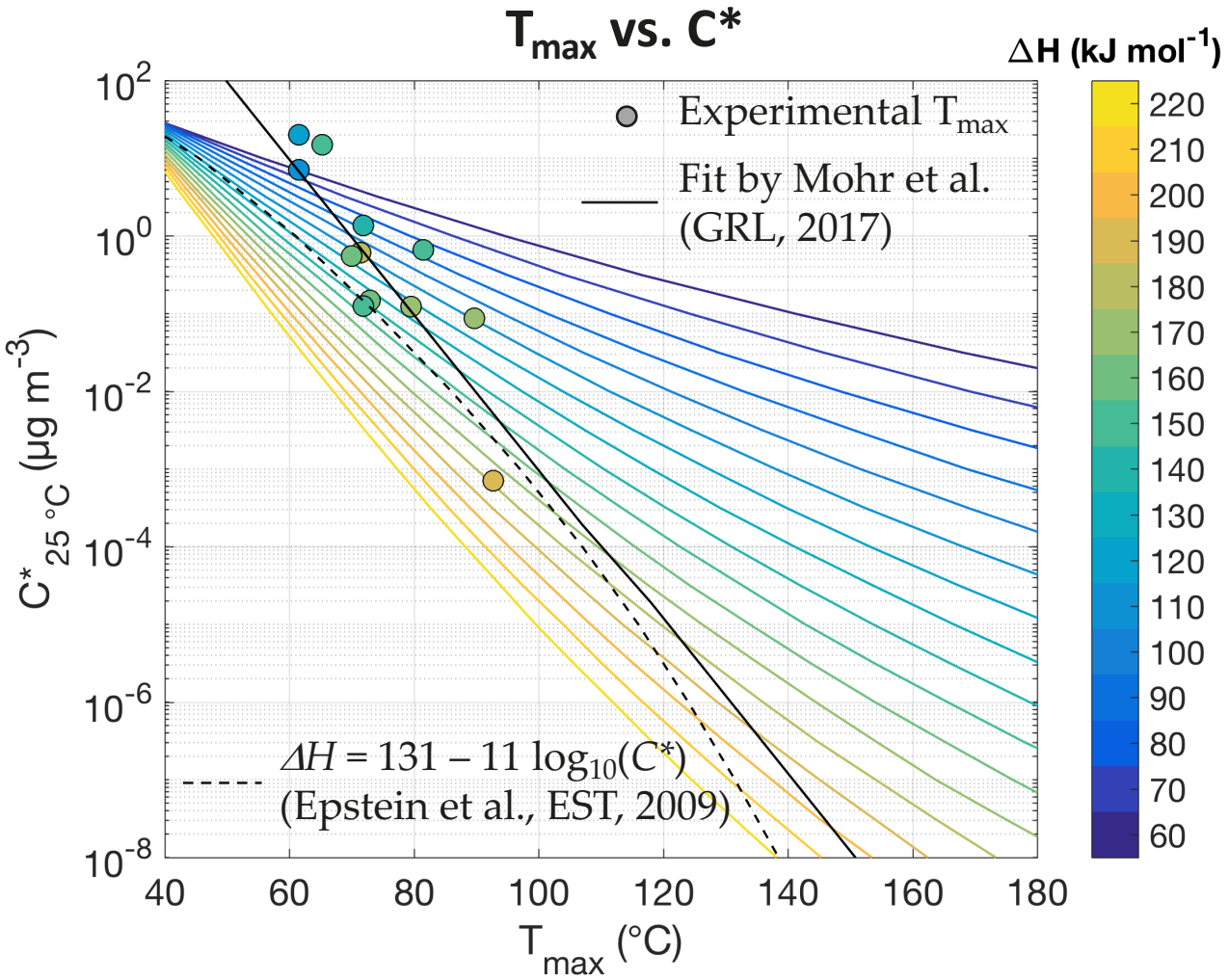


0.25	60
C^* (µg m^{-3})	ΔH (kJ mol^{-1})
0.02	120
1×10^{-3}	133
5×10^{-5}	146

Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

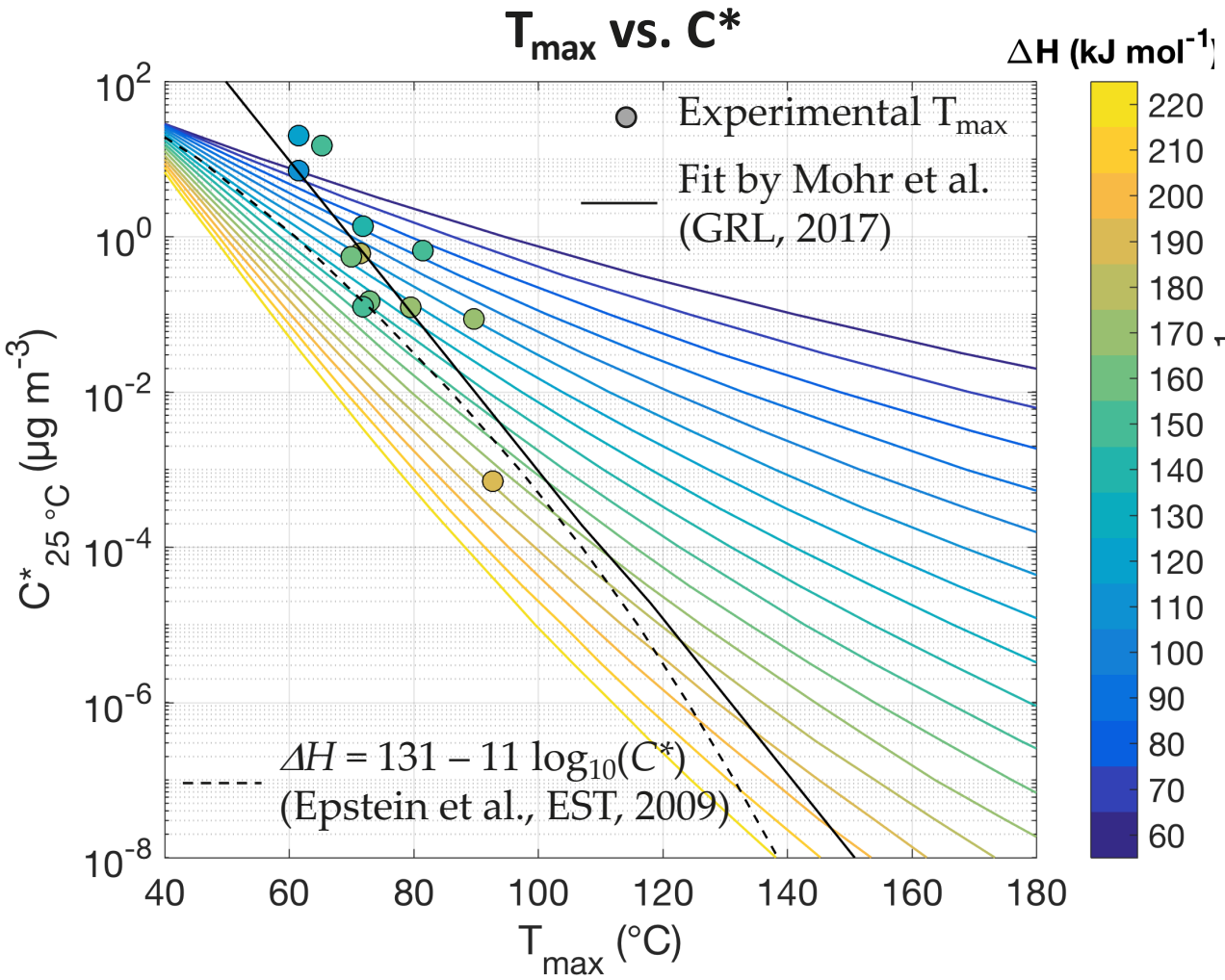
$$k_{des} = f \cdot C^*_{i,0} \cdot e^{-\frac{\Delta H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}$$

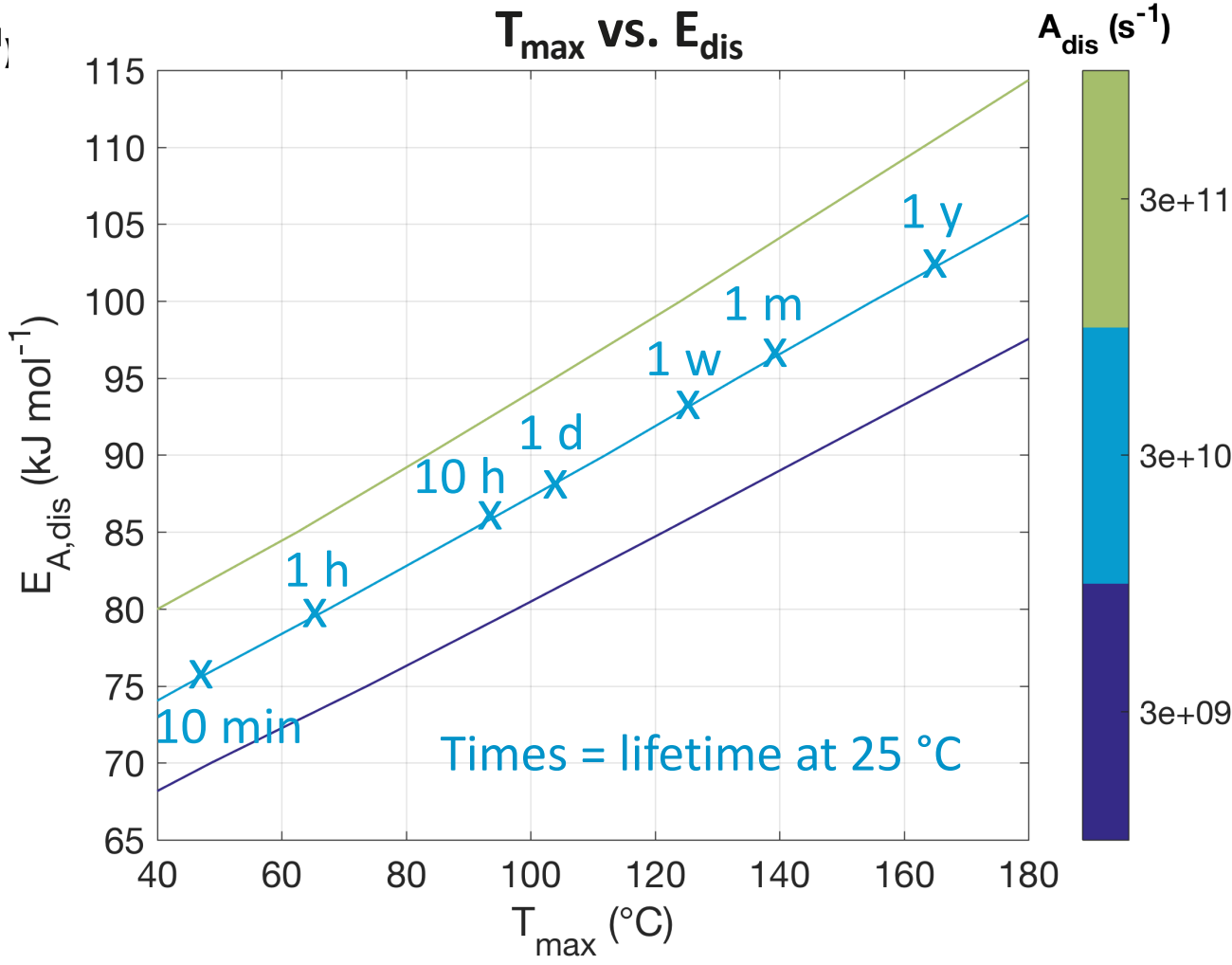


Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

$$k_{des} = f \cdot C^*_{i,0} \cdot e^{-\frac{\Delta H}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \longrightarrow k_{des} = A_{dis} \cdot e^{-\frac{E_A}{RT}}$$

13 billion years
@ 160 kJ/mol

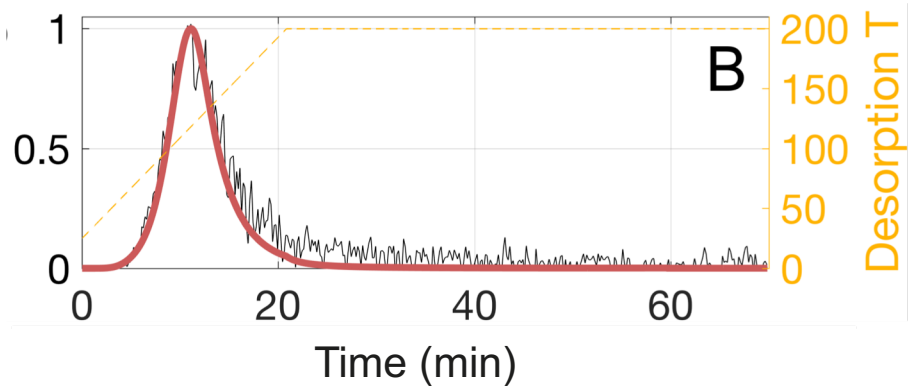




Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

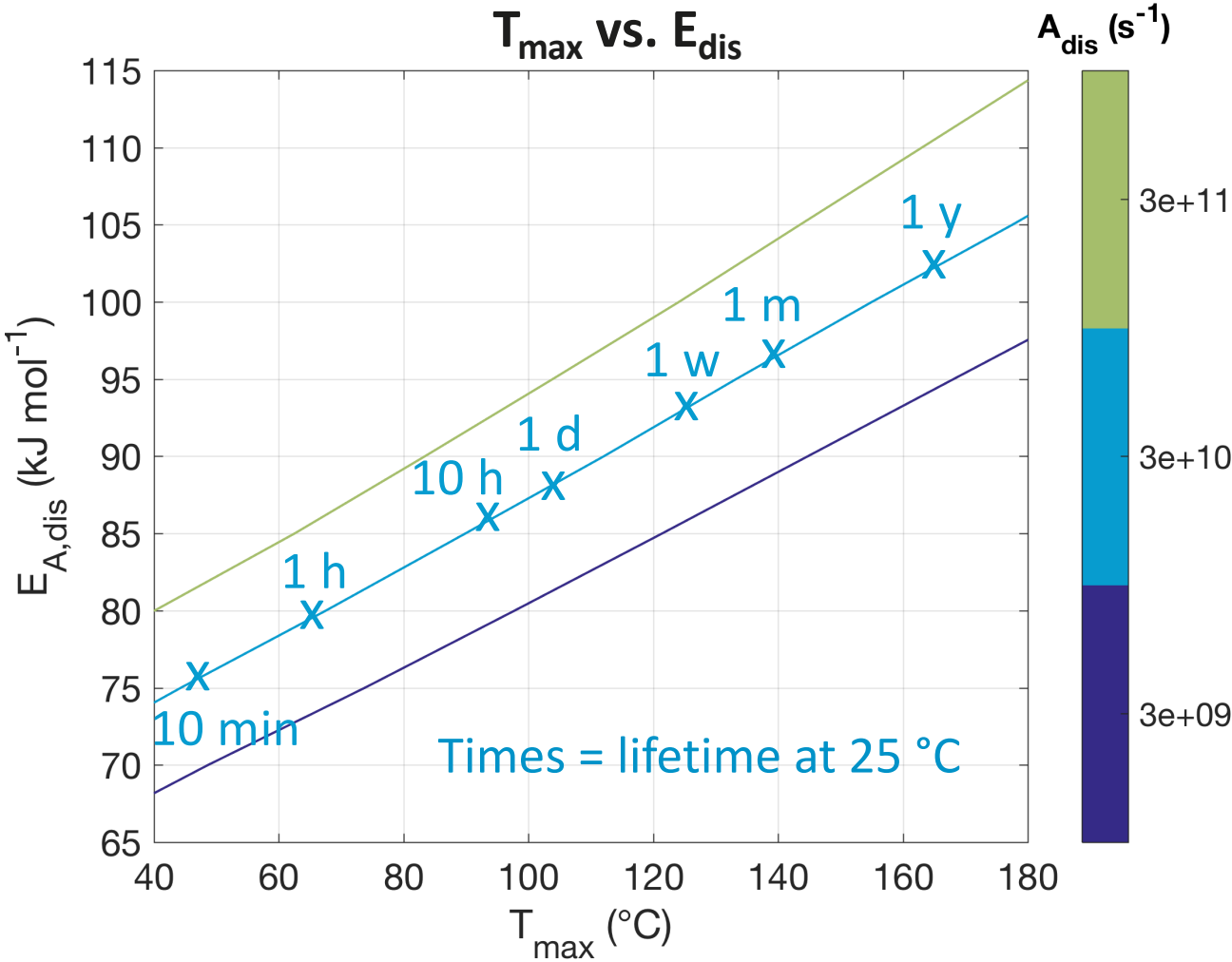
$$k_{des} = A_{dis} \cdot e^{-\frac{E_A}{RT}}$$

E.g.: $C_{18}H_{28}O_6$



~~C^* (µg m^{-3})~~	~~ΔH (kJ mol^{-1})~~
~~2e-1 to 5e-5~~	~~60 to 146~~
$k_{d\ (25C)}$ (s^{-1})	E_A (kJ mol^{-1})
2×10^{-6}	92

Lifetime = 6 d, $A_d = 3 \times 10^{10}$ s^{-1} (OK)



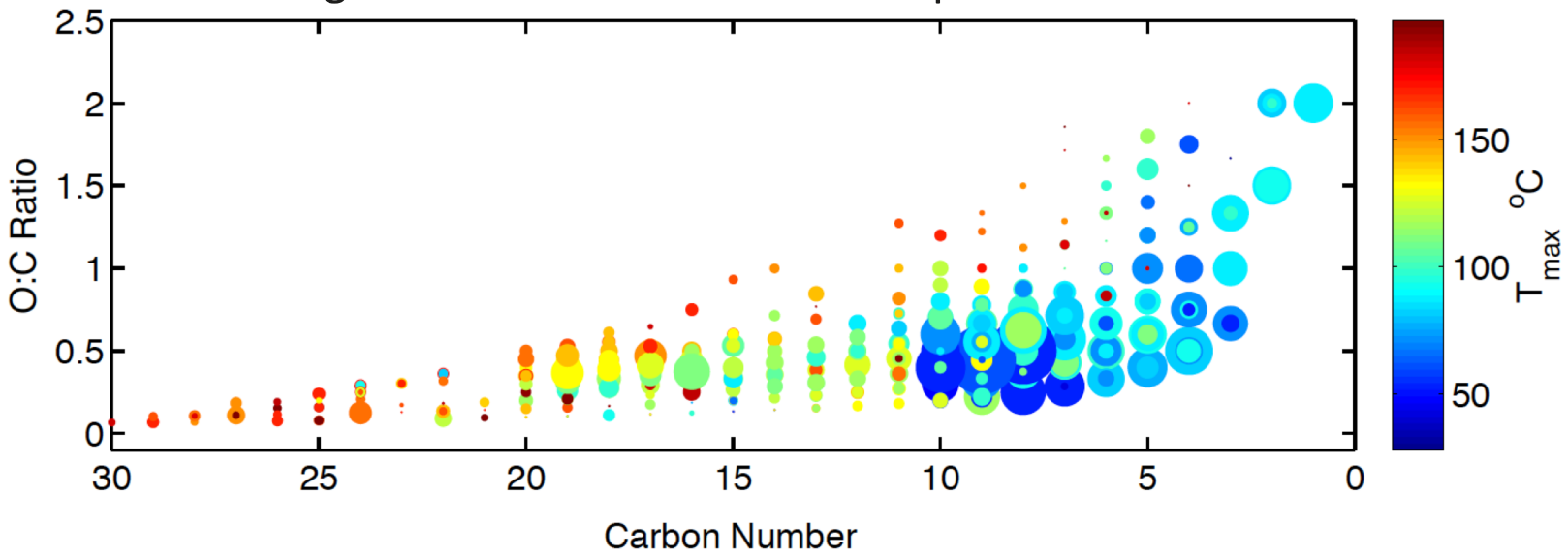
Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

?

Motivation:

- Many individual thermograms should be analyzed.

E.g.: α-Pinene SOA chamber experiment



Lopez-Hilfiker et al., ACP, 2015

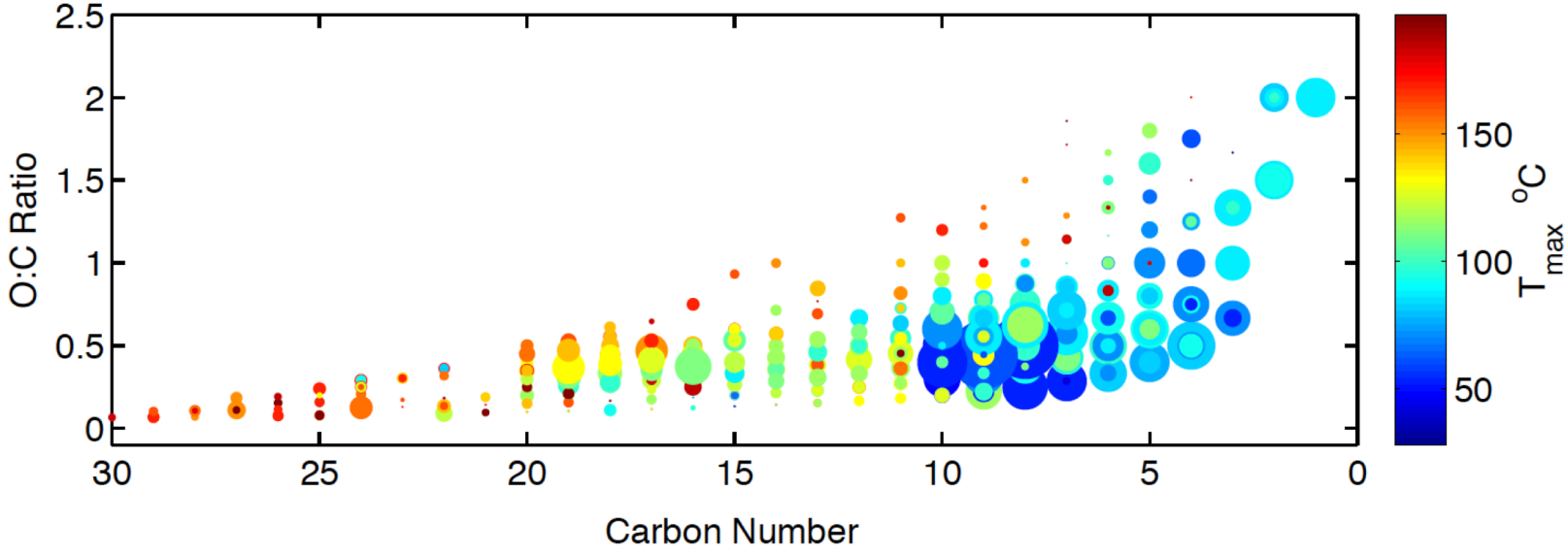
Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

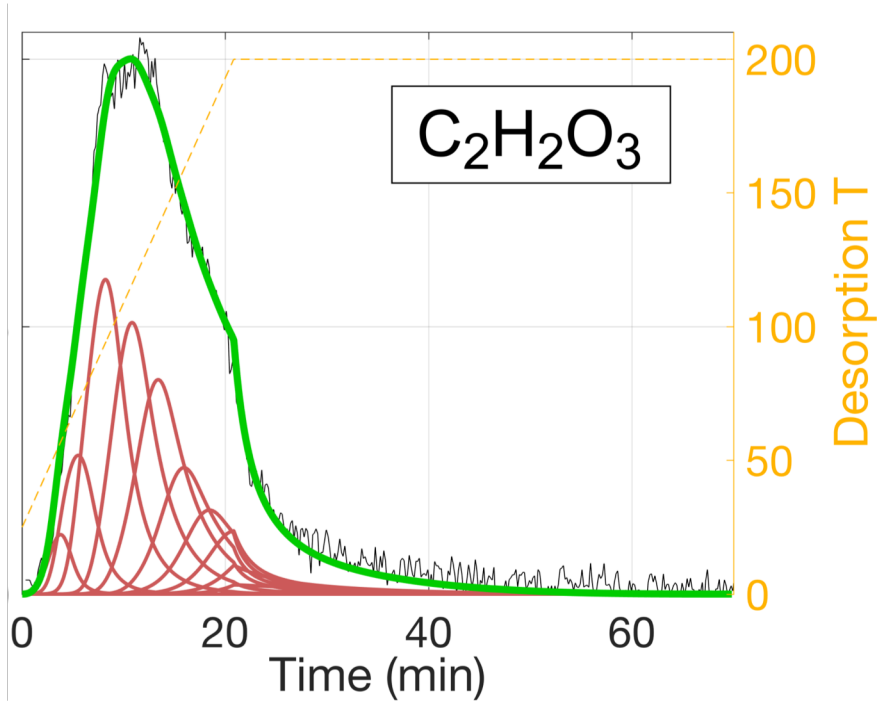
?

Motivation:

- Many individual thermograms should be analyzed.
- Complex thermogram shapes.

E.g.: α-Pinene SOA chamber experiment

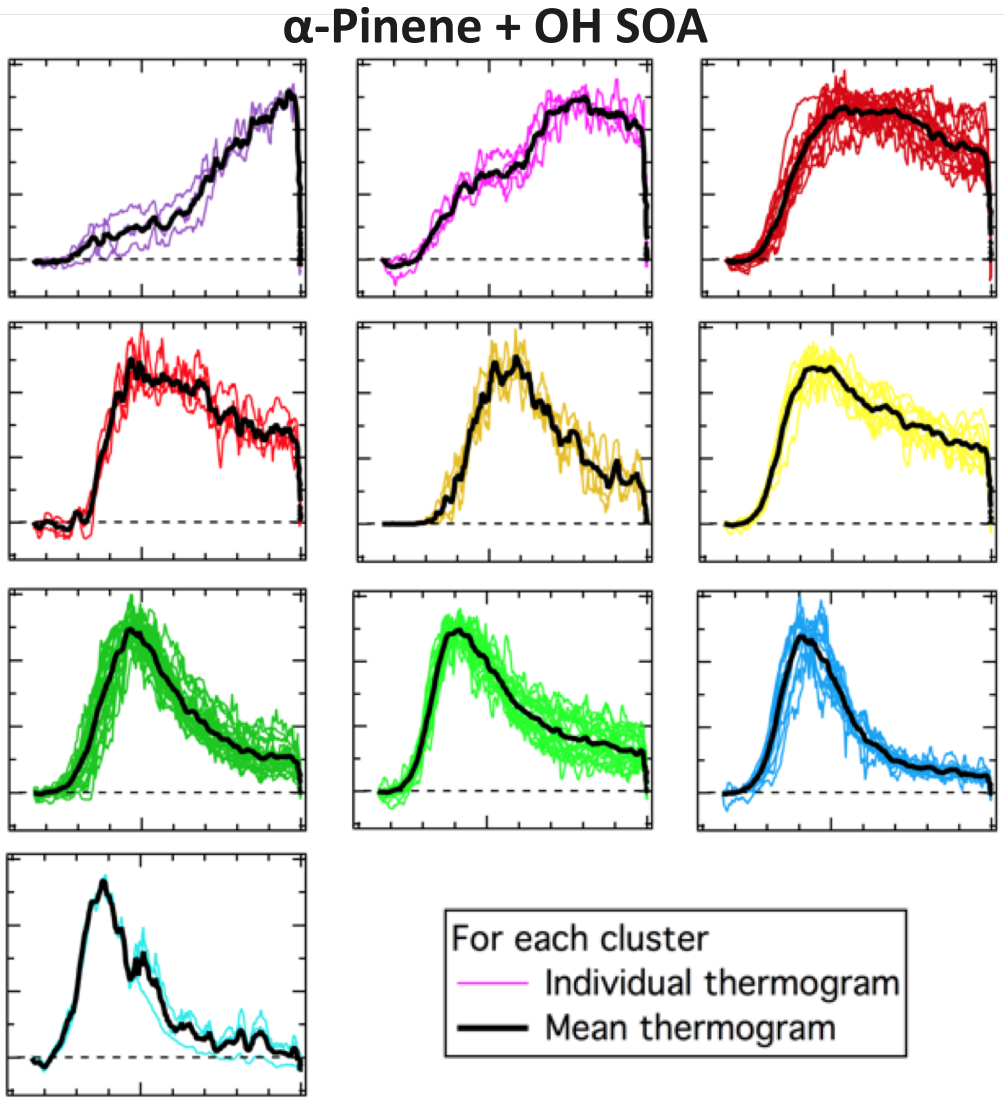




Lopez-Hilfiker et al., ACP, 2015

Step 1 (this time): “robust **clustering algorithm**” for thermograms

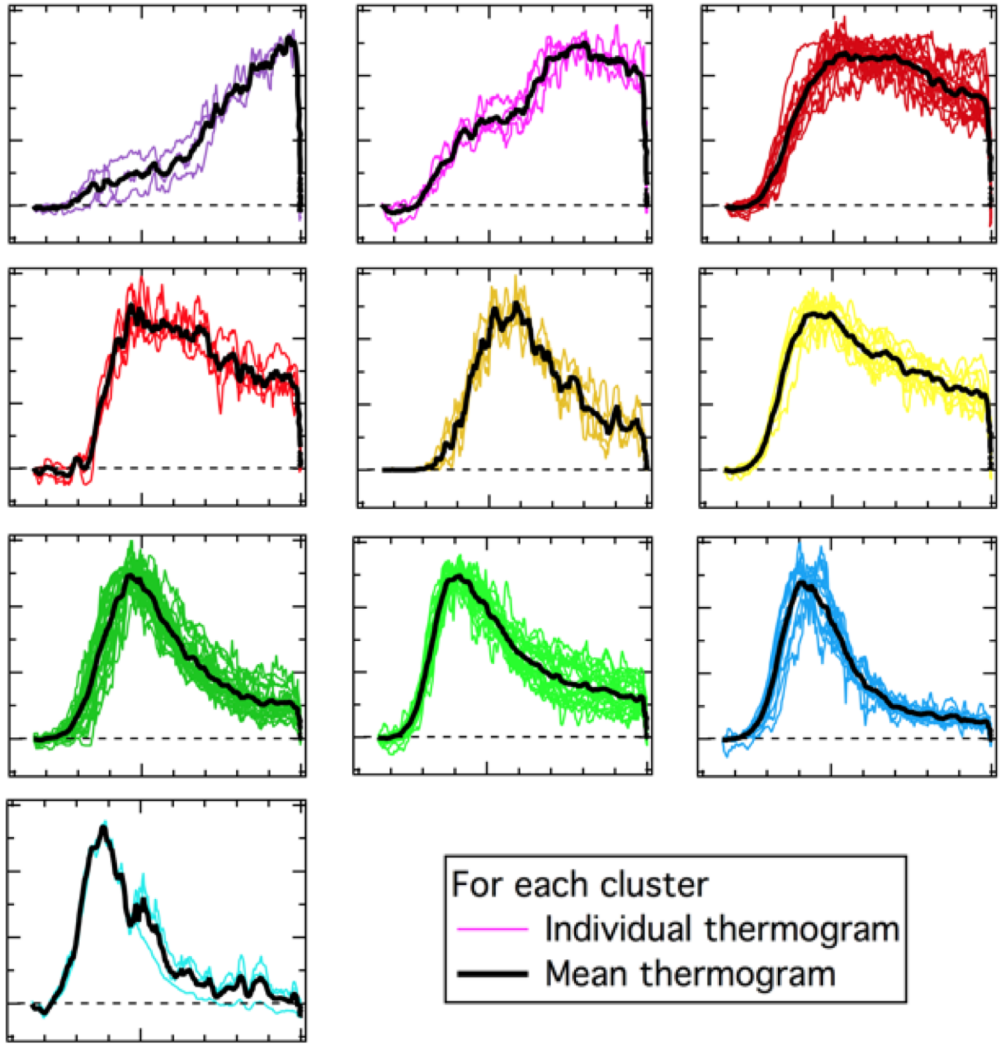
Ziyue **Li et al., ACPD, 2019** (10.5194/acp-2019-733)



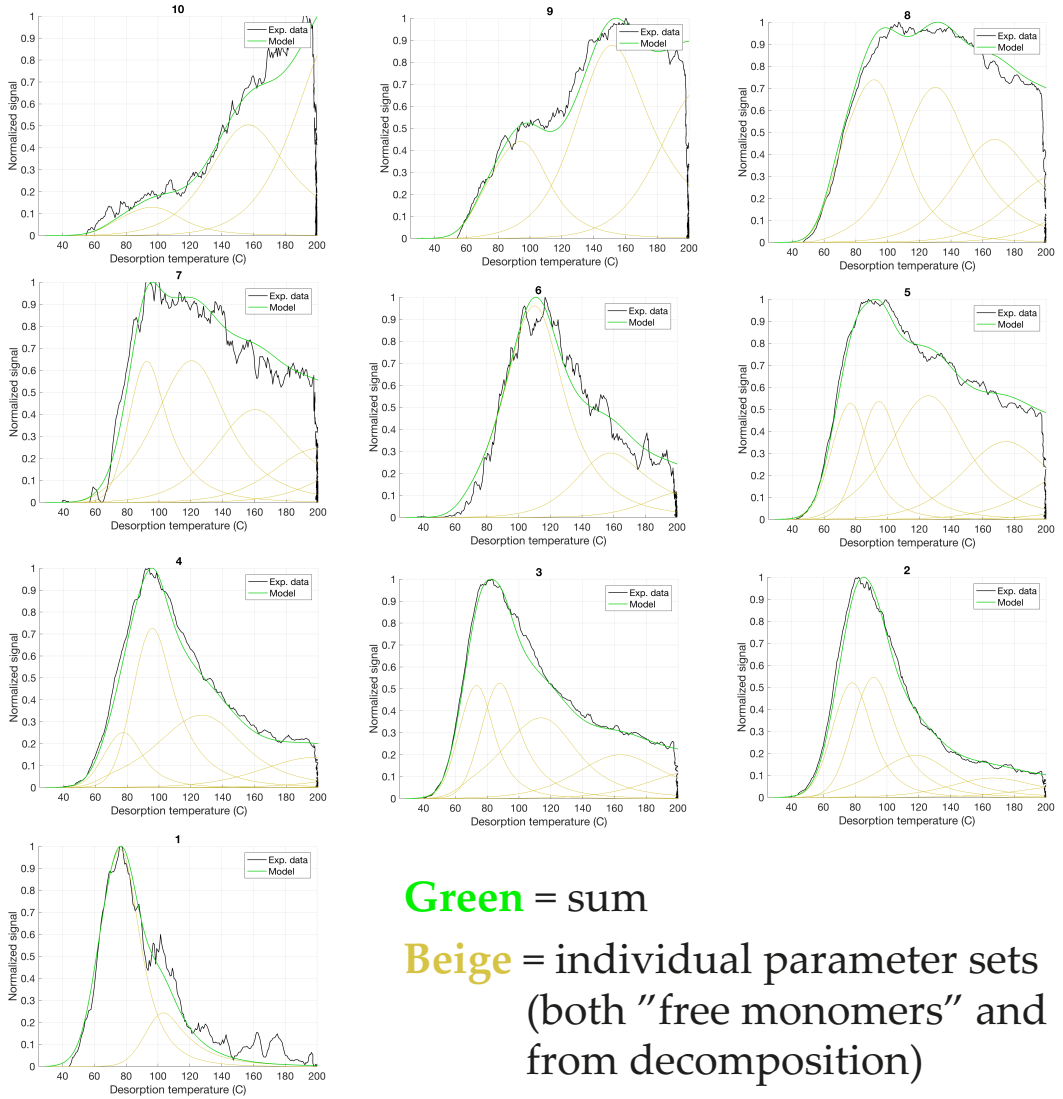
Step 1 (this time): “robust **clustering algorithm**” for thermograms

Ziyue **Li et al., ACPD, 2019** (10.5194/acp-2019-733)

α-Pinene + OH SOA



Manual ”expert” fitting results:

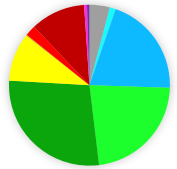


Green = sum

Beige = individual parameter sets (both ”free monomers” and from decomposition)

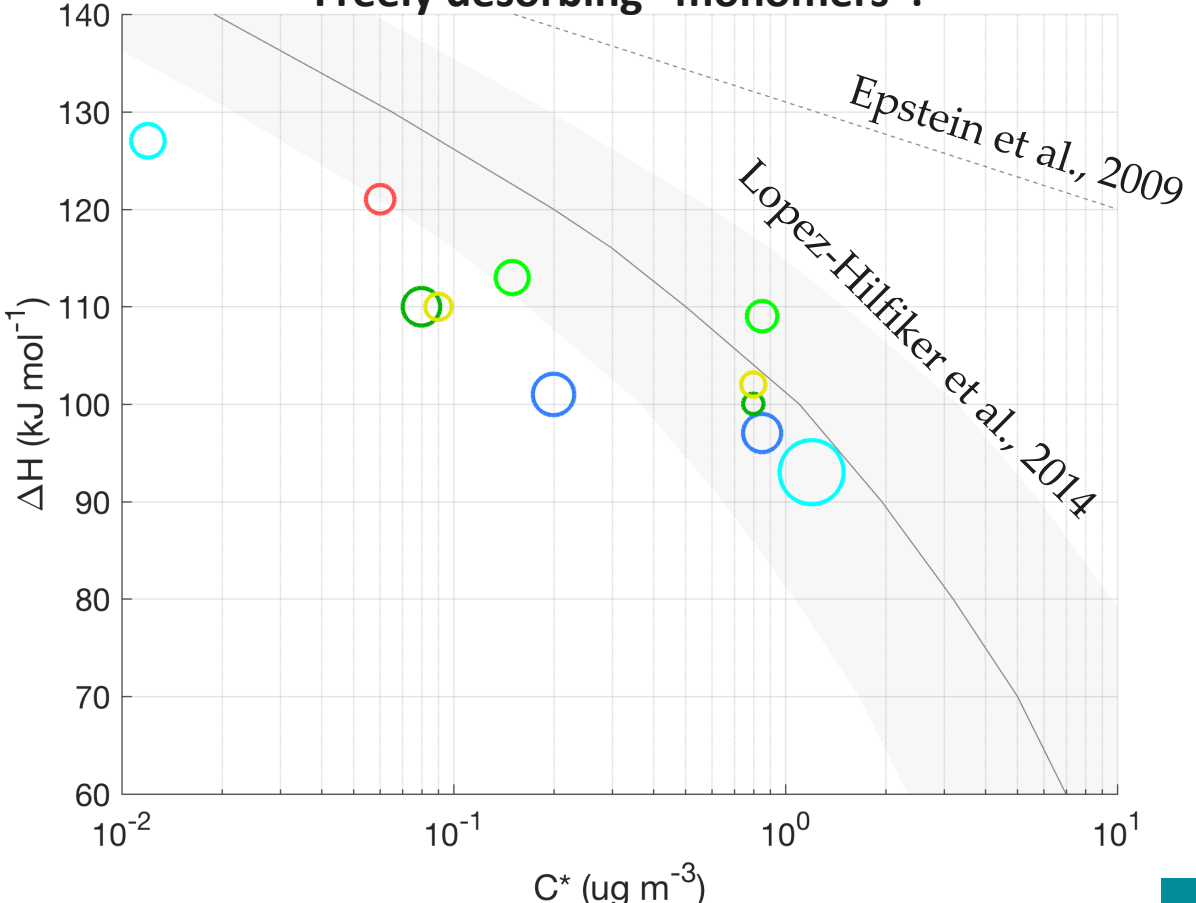
Manual “expert” fitting results for weighted-average cluster thermograms: **reference**

Relative contributions of clusters 1-10 (Li et al., 2019):

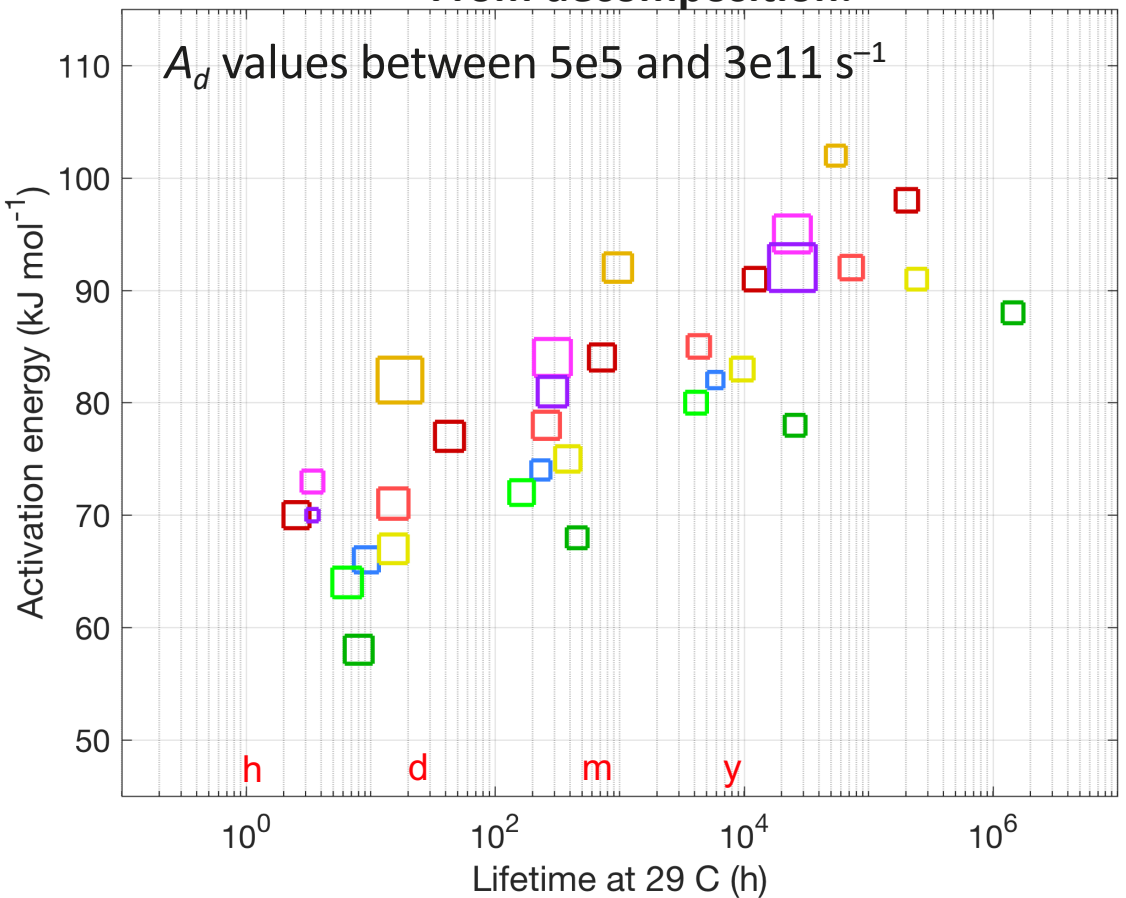


Epstein: $\Delta H = 131 - 11 \log_{10}(C^*)$
Lopez-Hilfiker: literature-based

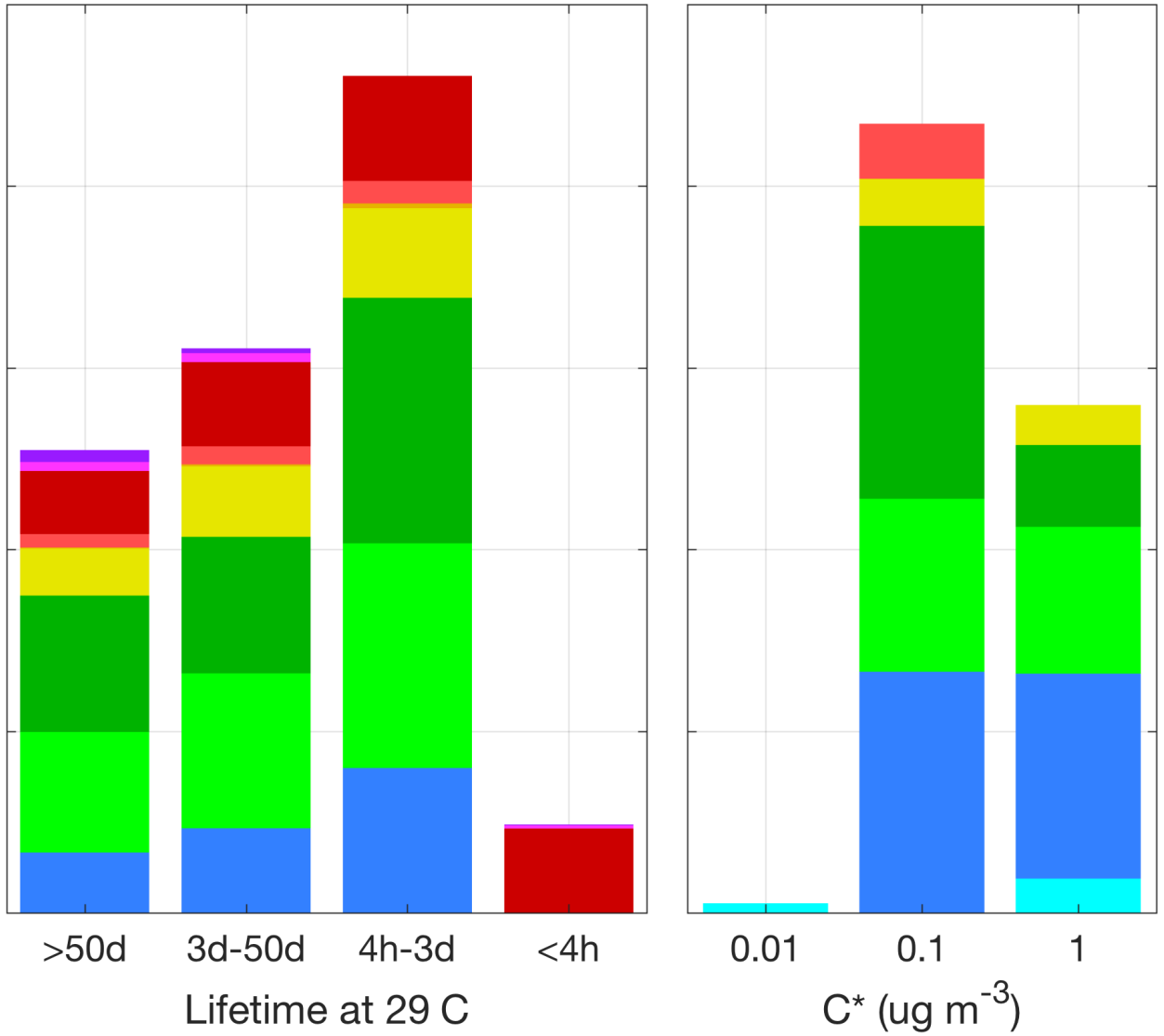
Freely desorbing “monomers”:



From decomposition:



Manual “expert” fitting results for weighted-average cluster thermograms: **reference**



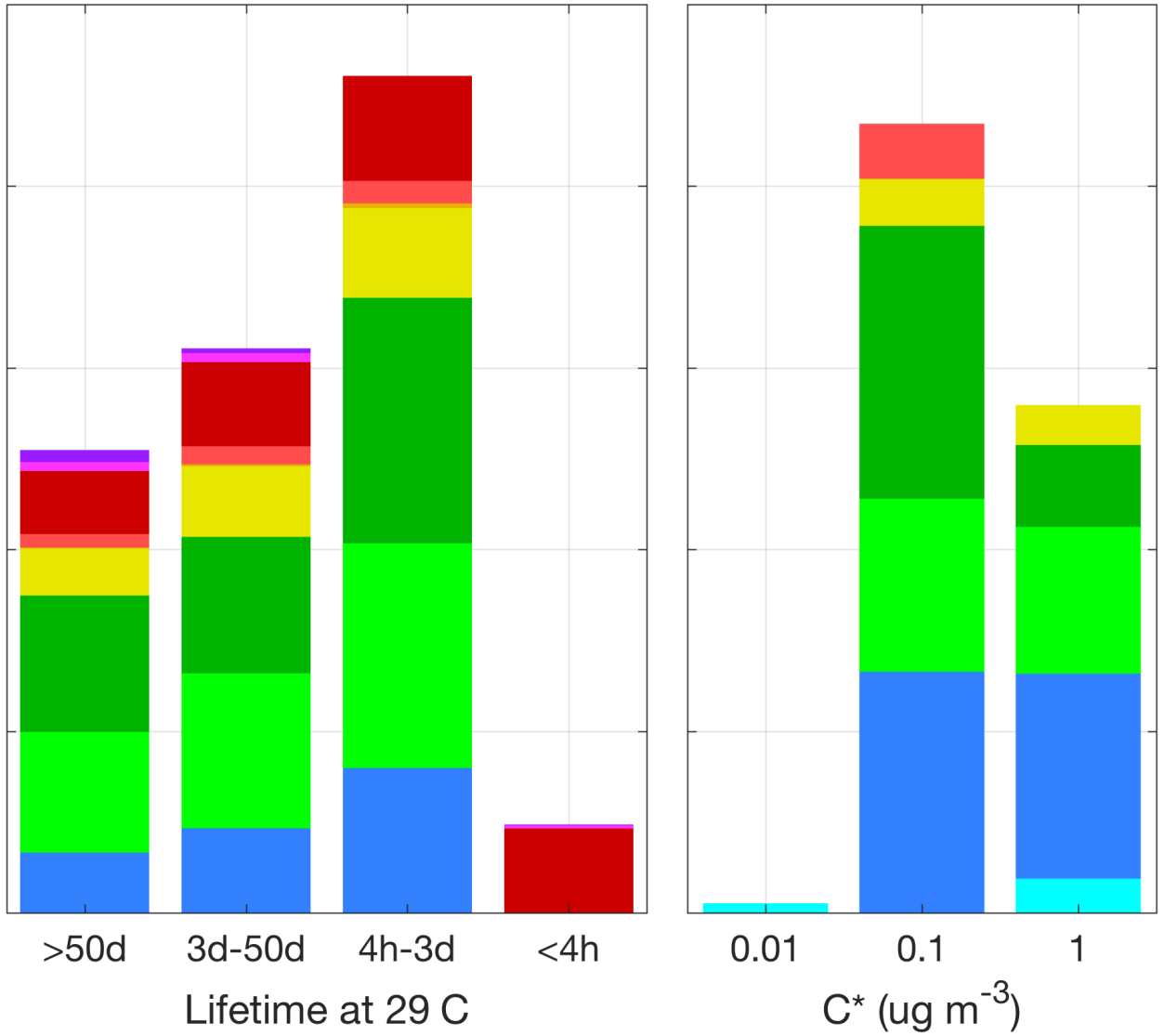
Manual “expert” fitting results for weighted-average cluster thermograms: **reference**

Took me 1-2 work days...

Could my (or a) computer do that work on its own?

- **Unattended**
- **Maybe also faster**
- **Better usability?**

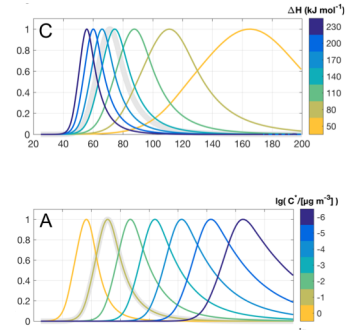
Also:
Let’s determine **upper-limit C*** for decomposing parent compounds.



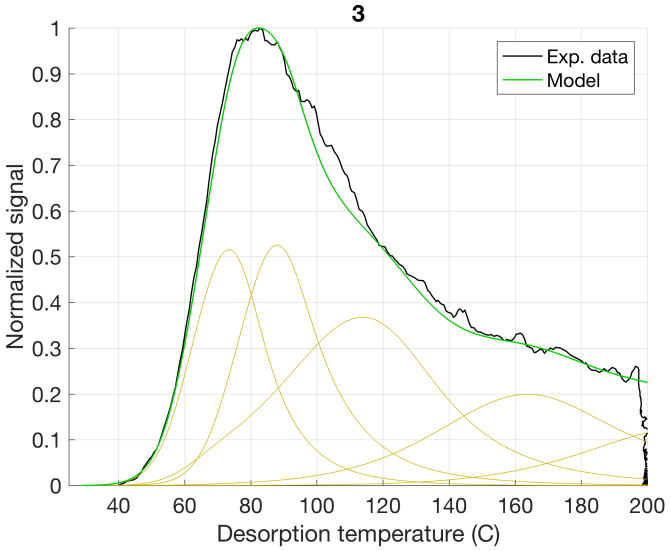
Automatic thermogram fitting: **overall strategy** ... piece-wise fitting!

WHY:

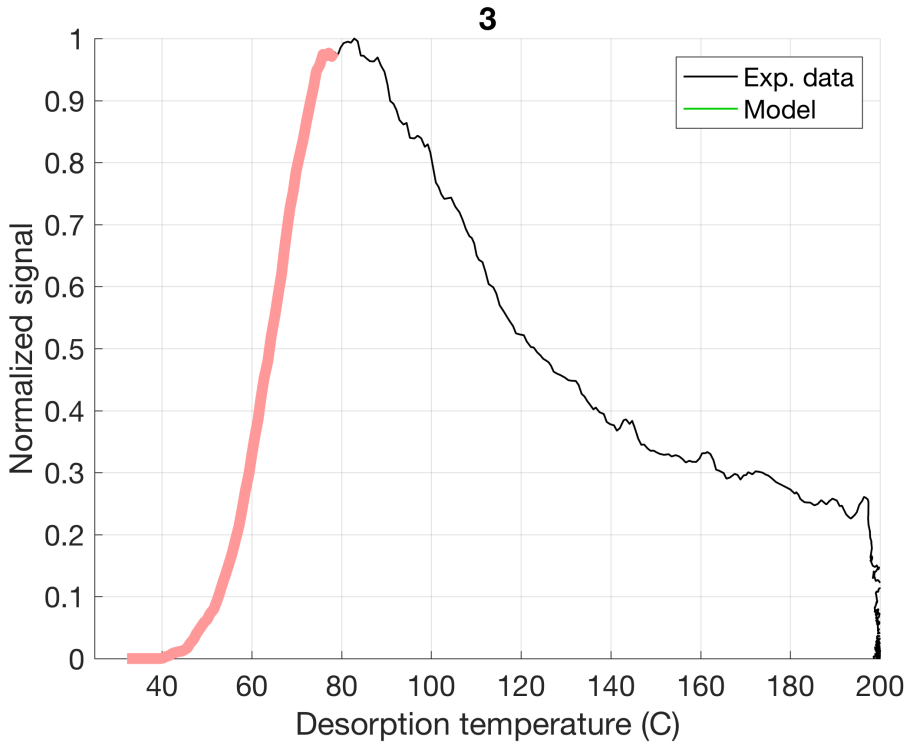
- Typically, **initial upslope** of a thermogram is a tight **constraint on ΔH**
- **Location in temperature space** (of that upslope) then **constrains C*$_0$**



E.g. cluster #3:



Start with fitting one peak to the initial upslope:



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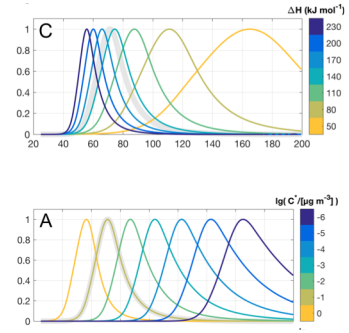

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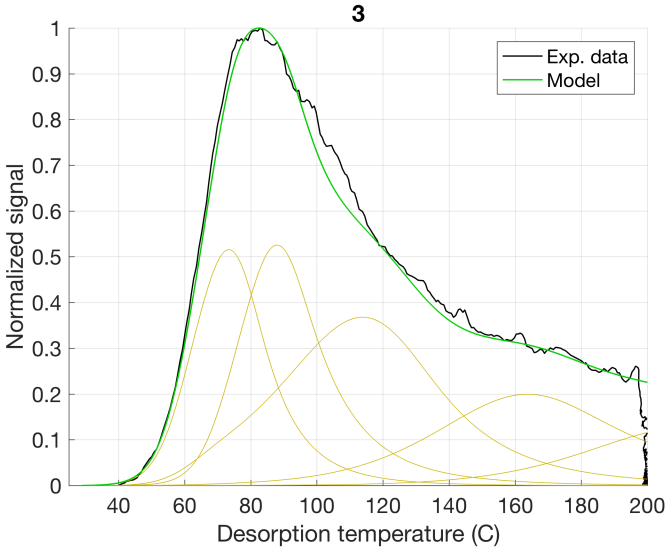

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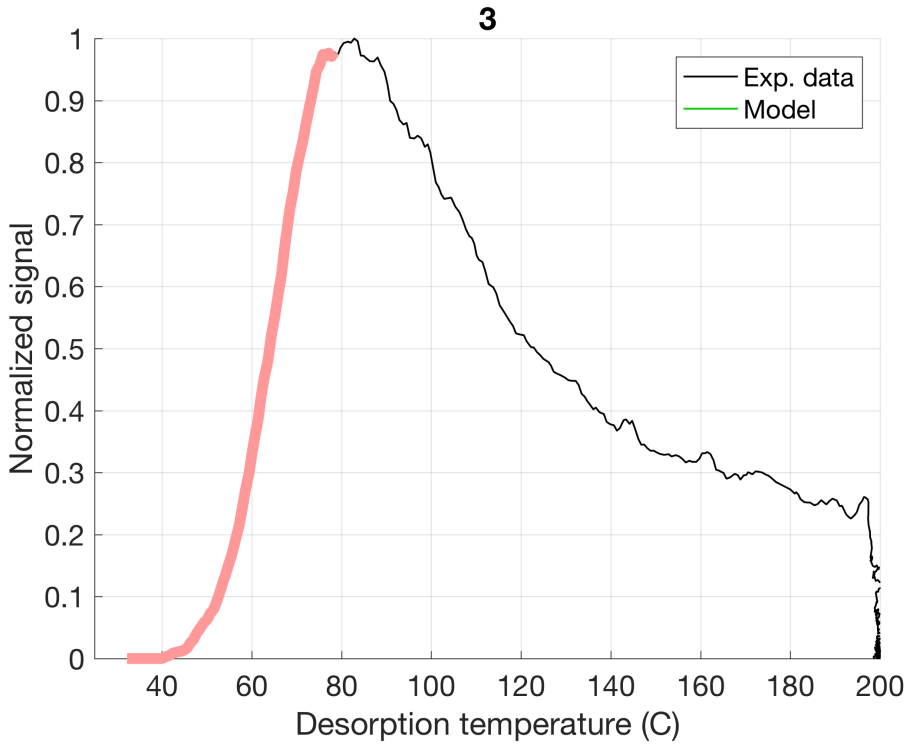

Identified using a **peak finding routine** adapted from "tofTools".
Includes shoulder detection, based on O'Haver (et al.)'s work (multiplying by derivatives).

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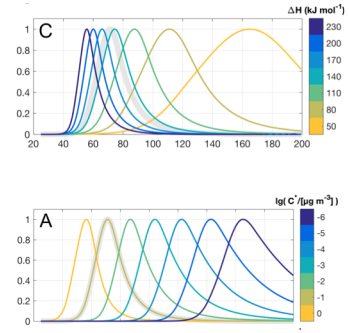

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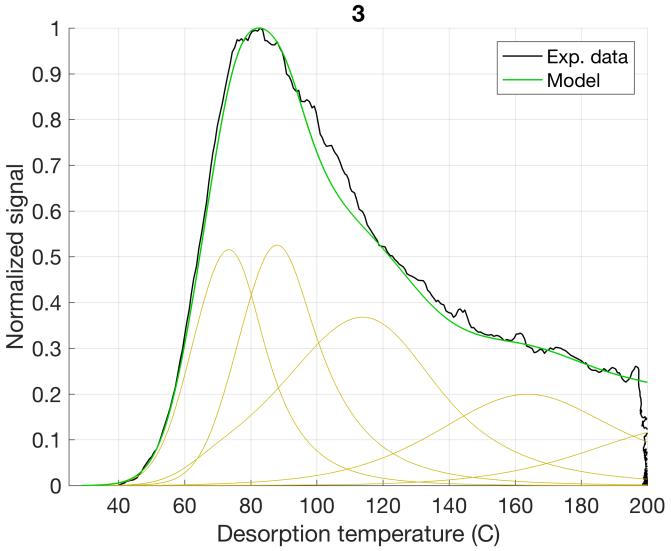

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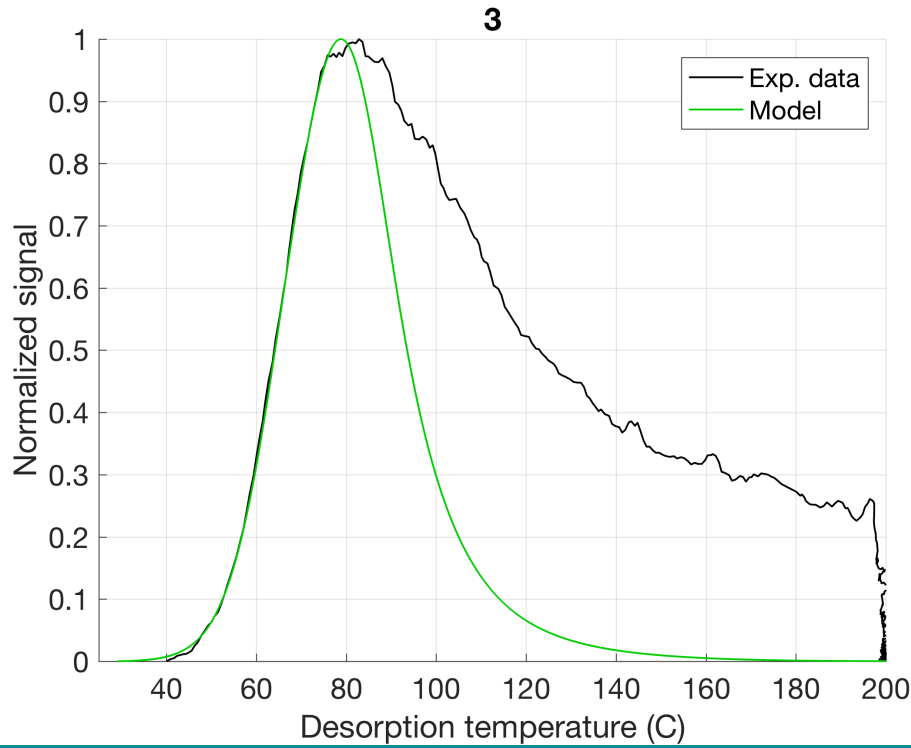

C^*_0 = 0.8 µg m^{-3}

ΔH = 97 kJ mol^{-1}

Automatic thermogram fitting: **overall strategy** … piece-wise fitting!

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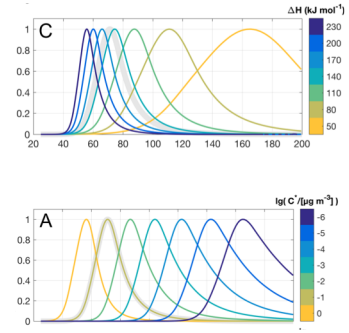

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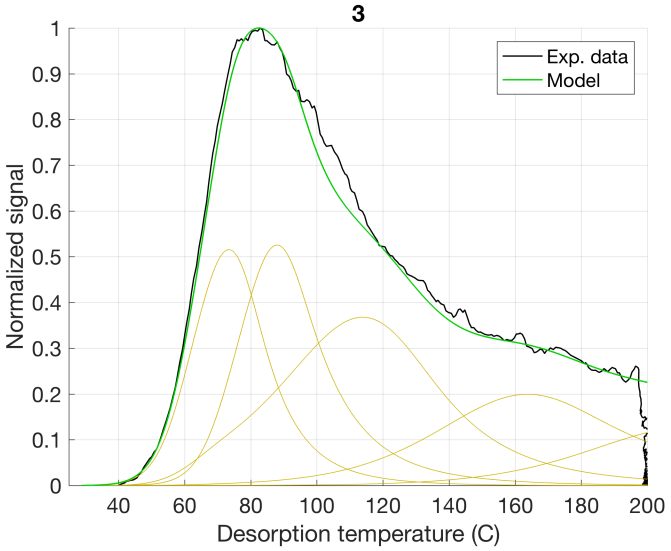

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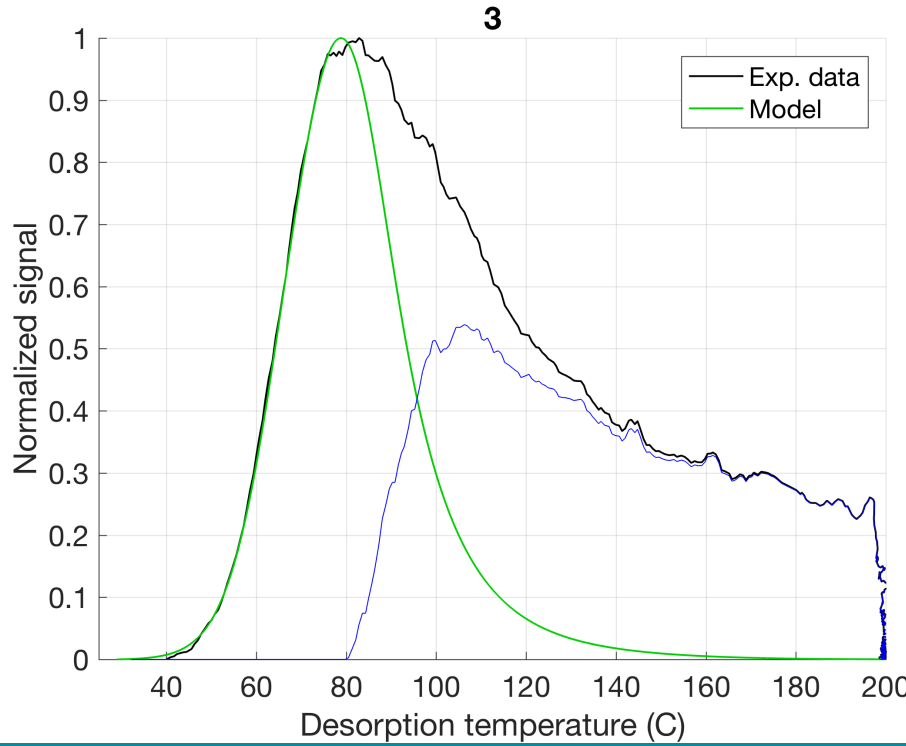

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- In residual (blue): find next peak

Automatic thermogram fitting: **overall strategy** … piece-wise fitting!

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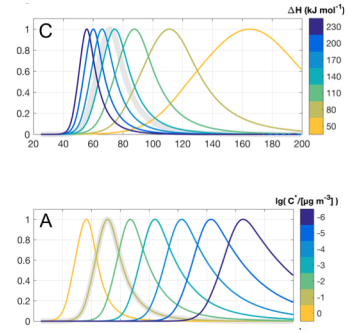

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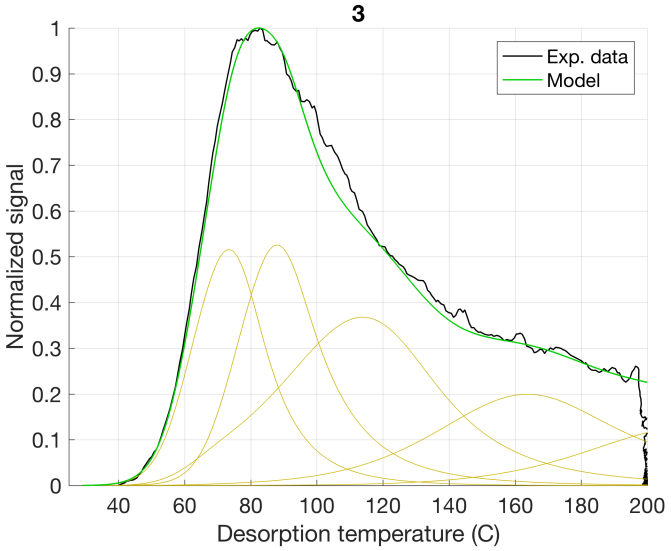

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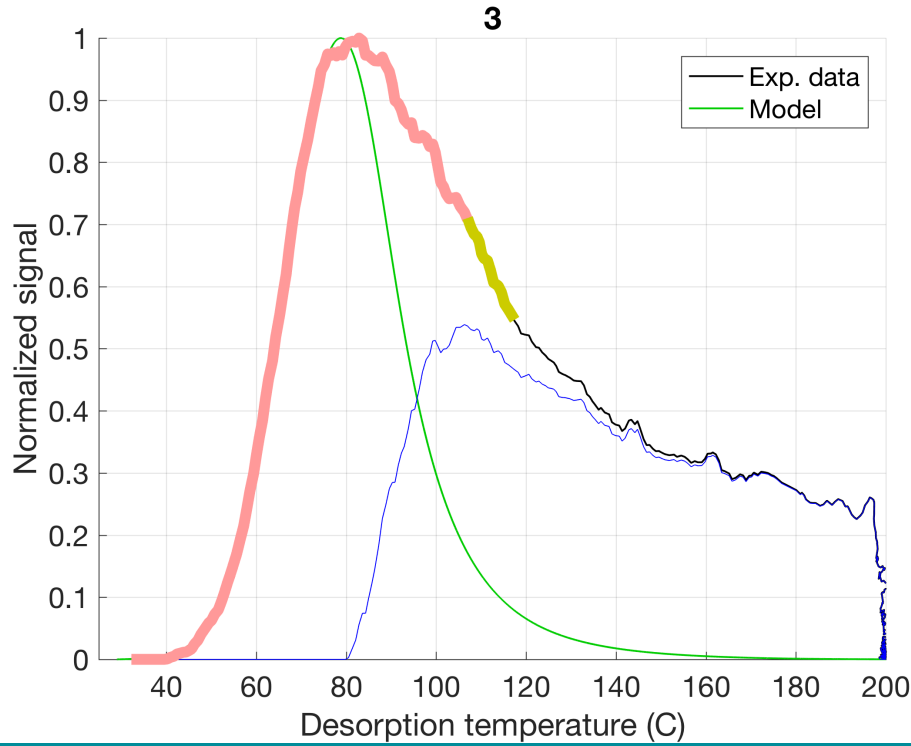

C^*_0 = 0.8 µg m^{-3}

ΔH = 97 kJ mol^{-1}

- In residual (blue): find next peak
- Define new fitting region (+ some)

Automatic thermogram fitting: **overall strategy** … piece-wise fitting!

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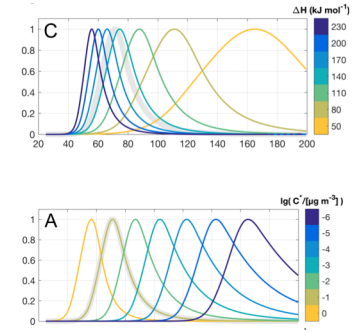

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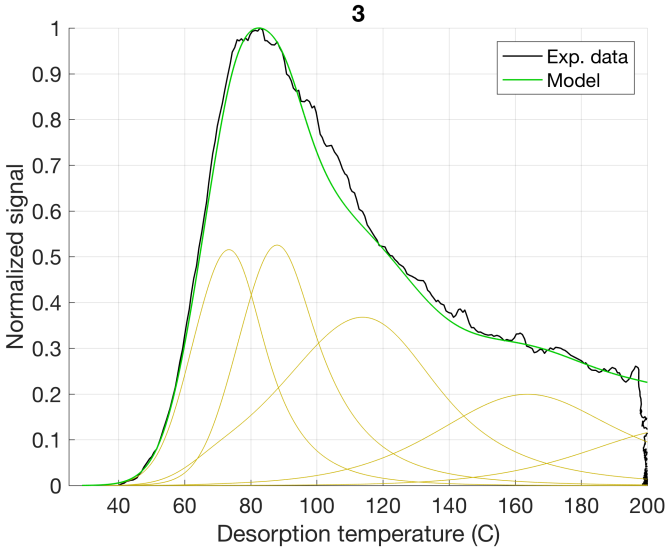
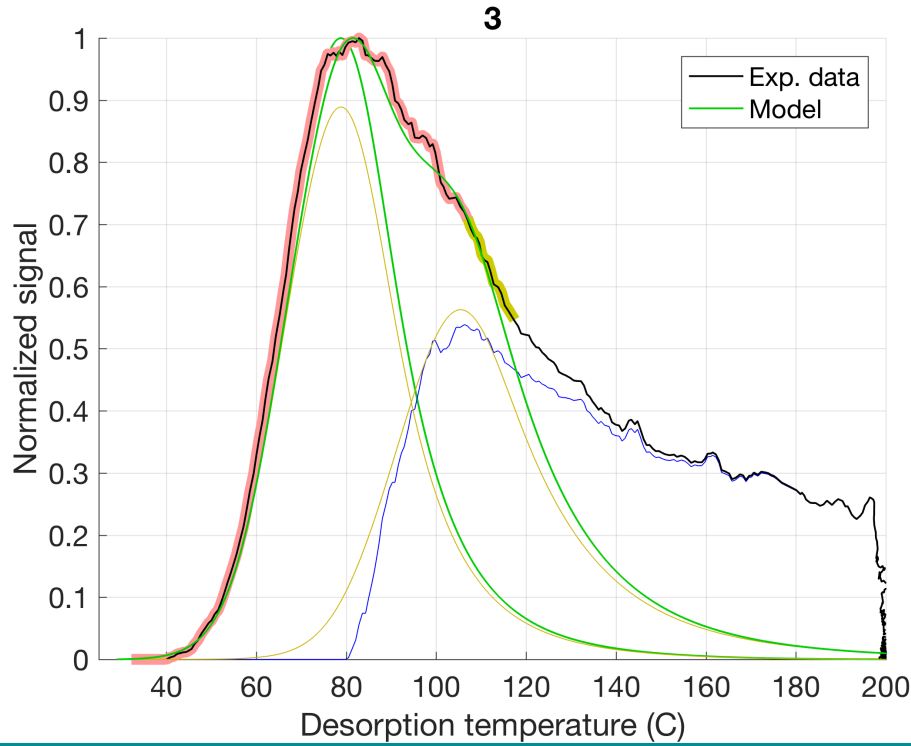


Start with fitting one peak to the initial upslope …

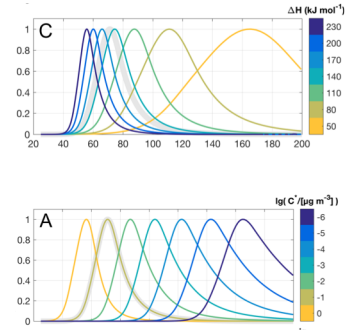


C^*_0 = 0.8 µg m^{-3}
ΔH = 97 kJ mol^{-1}
1st peak

- In residual (blue): find next peak
- Define new fitting region (+ some)

C^*_0 = 0.06 µg m^{-3}
ΔH = 101 kJ mol^{-1} *2nd peak*
N_2:N_1 = 0.80

Automatic thermogram fitting: **overall strategy** … piece-wise fitting!



WHY:

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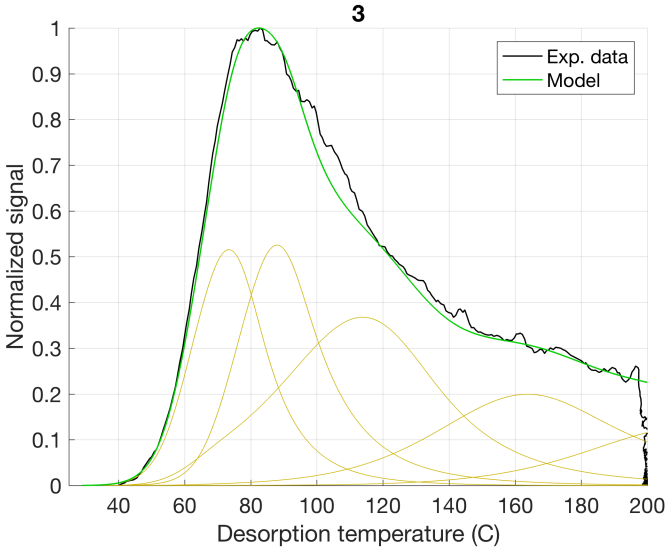
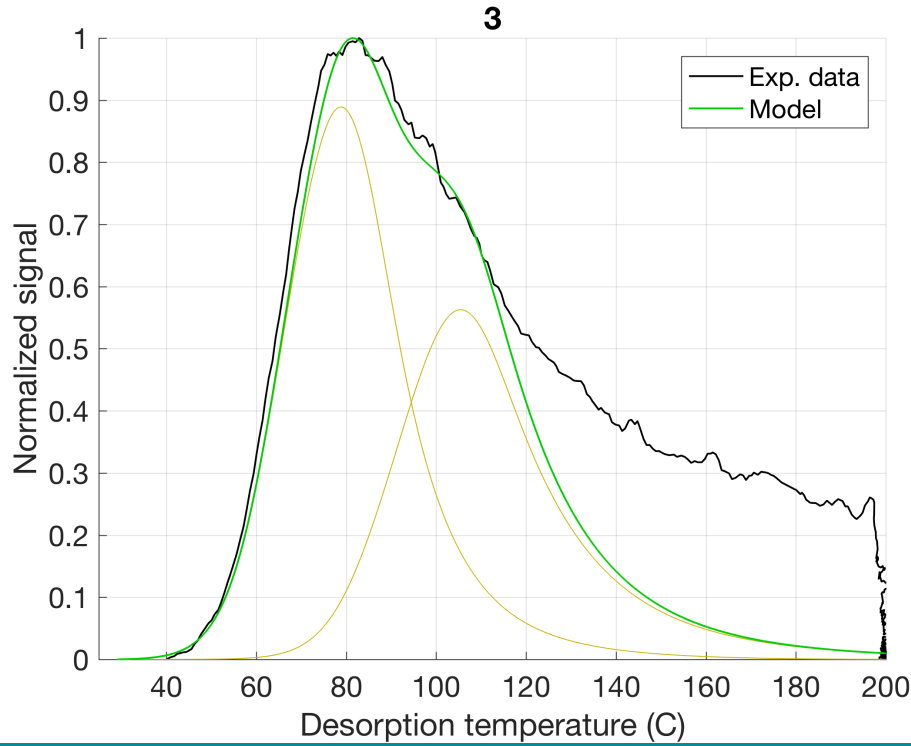


Start with fitting one peak to the initial upslope …



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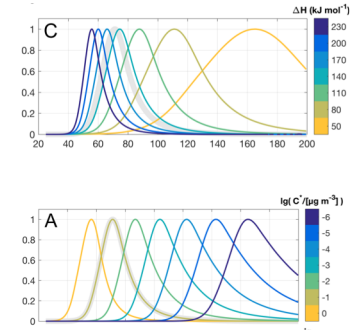

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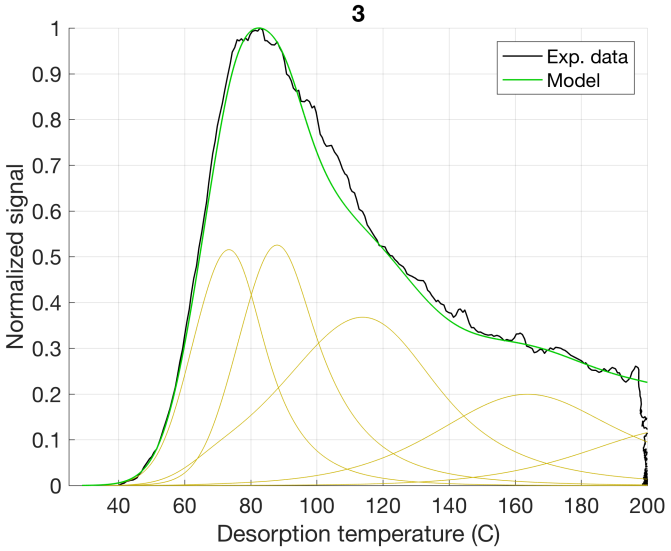

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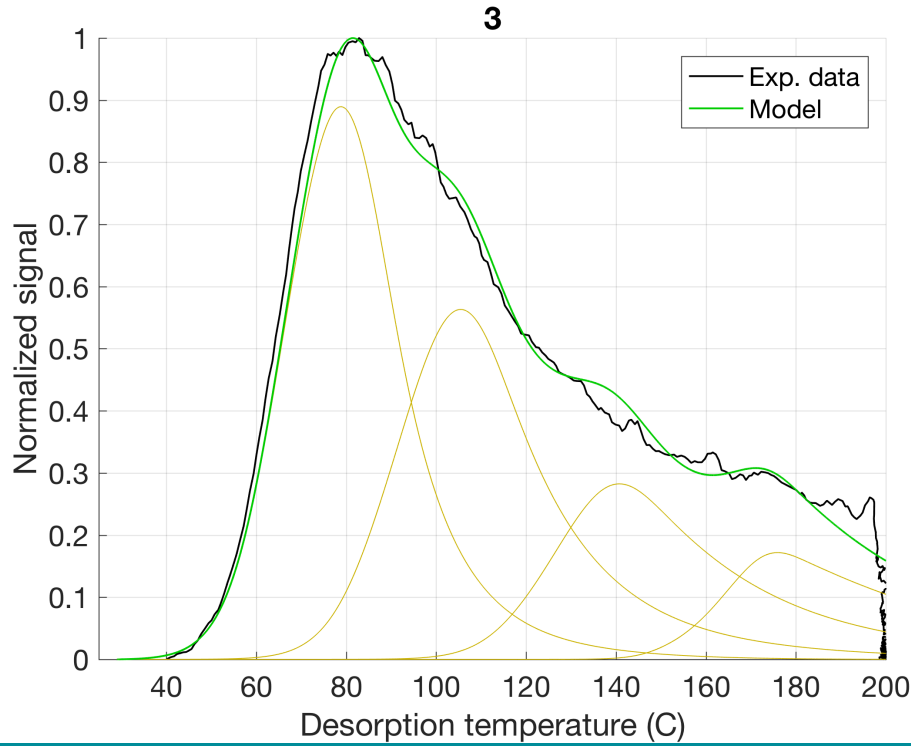

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And so on …

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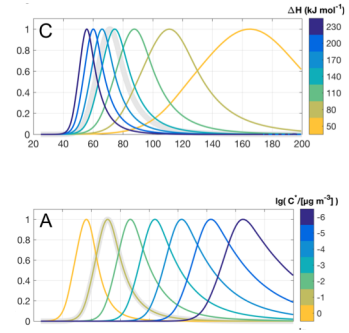

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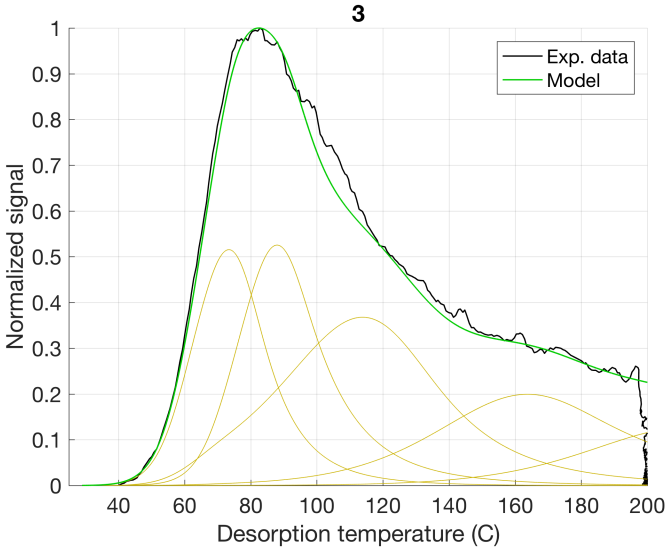

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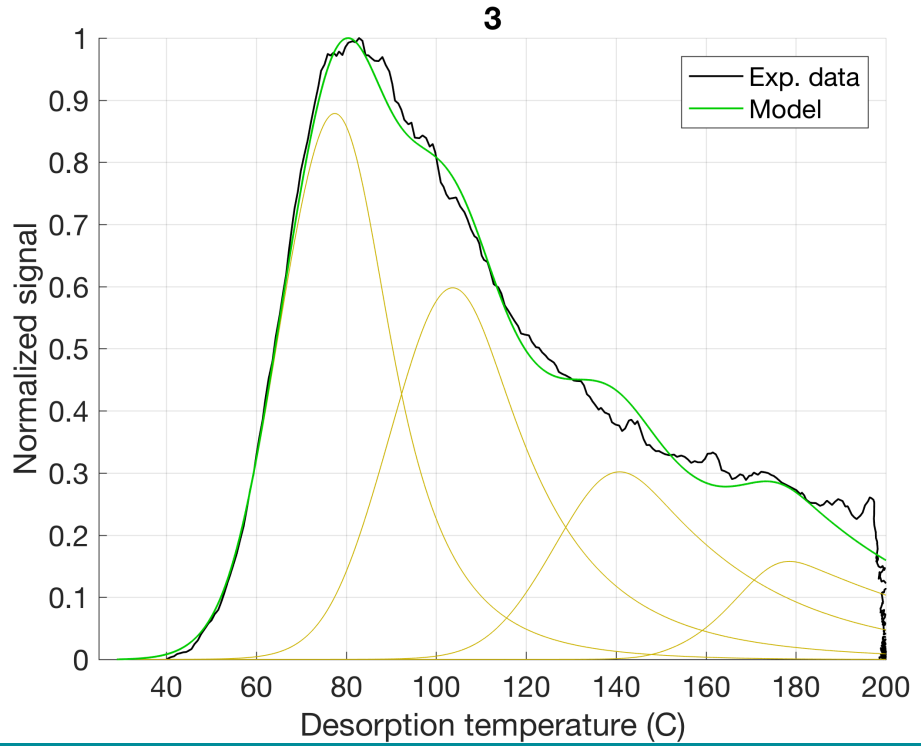
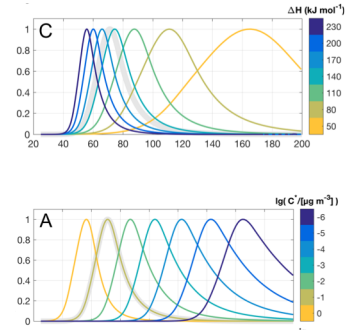


And so on …

Finishing with a final tweak of all C^*_0 and N (i.e., #(peaks)*2 free parameters) …

C^*_0 (μg m^{-3})	ΔH (kJ mol^{-1})	N/N_{tot}
0.9	97	0.36
0.07	101	0.31
4e–4	123	0.20
4e–9	190	0.12

Automatic thermogram fitting: **overall strategy** ... piece-wise fitting!



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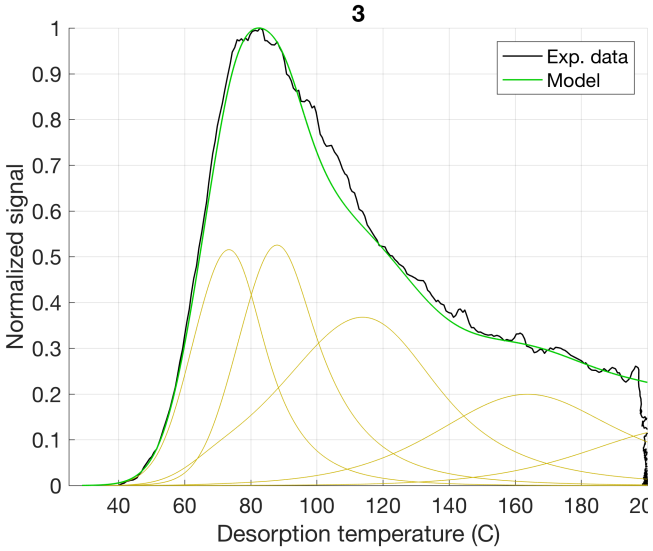
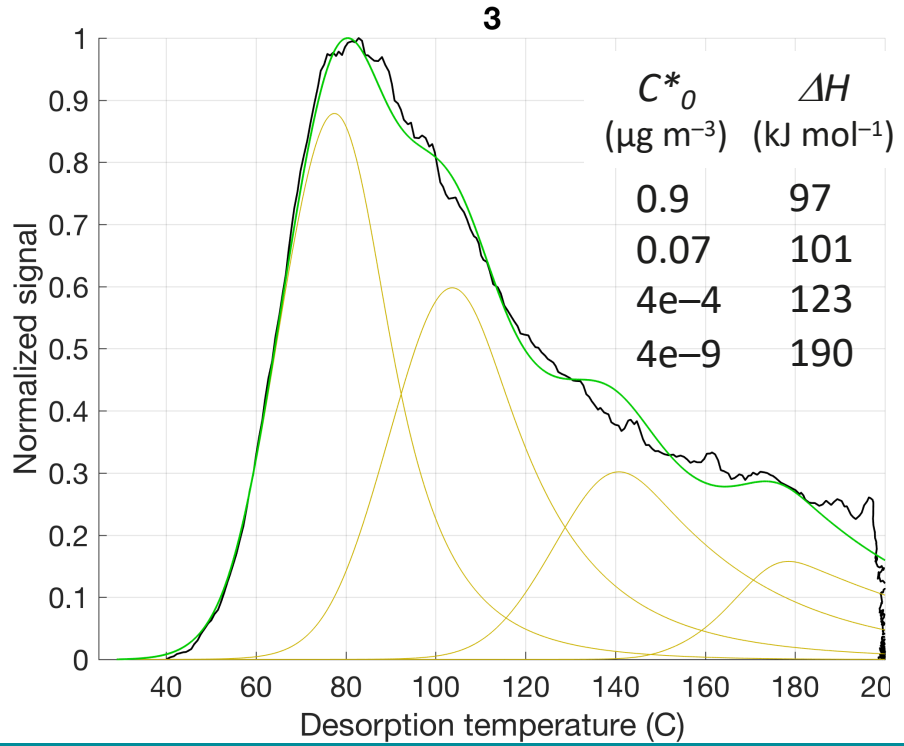
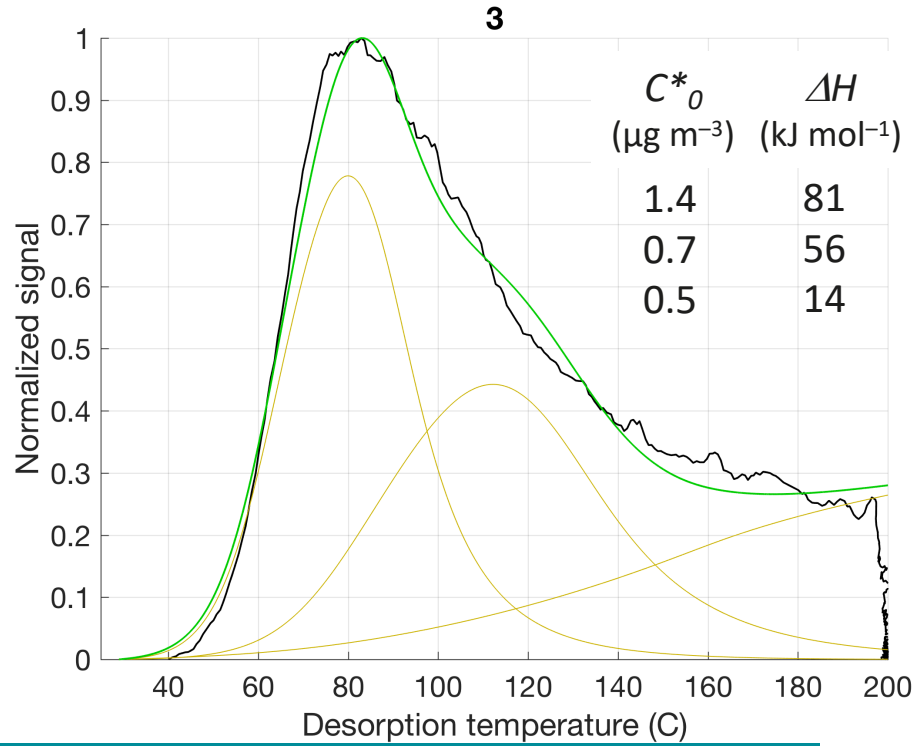


Solutions of the routine not unique, but usually (not here) quite similar:





Automatic thermogram fitting: **CMA-ES as optimizer**

(CMA-ES = Covariance Matrix Adaptation – Evolutionary Strategy)

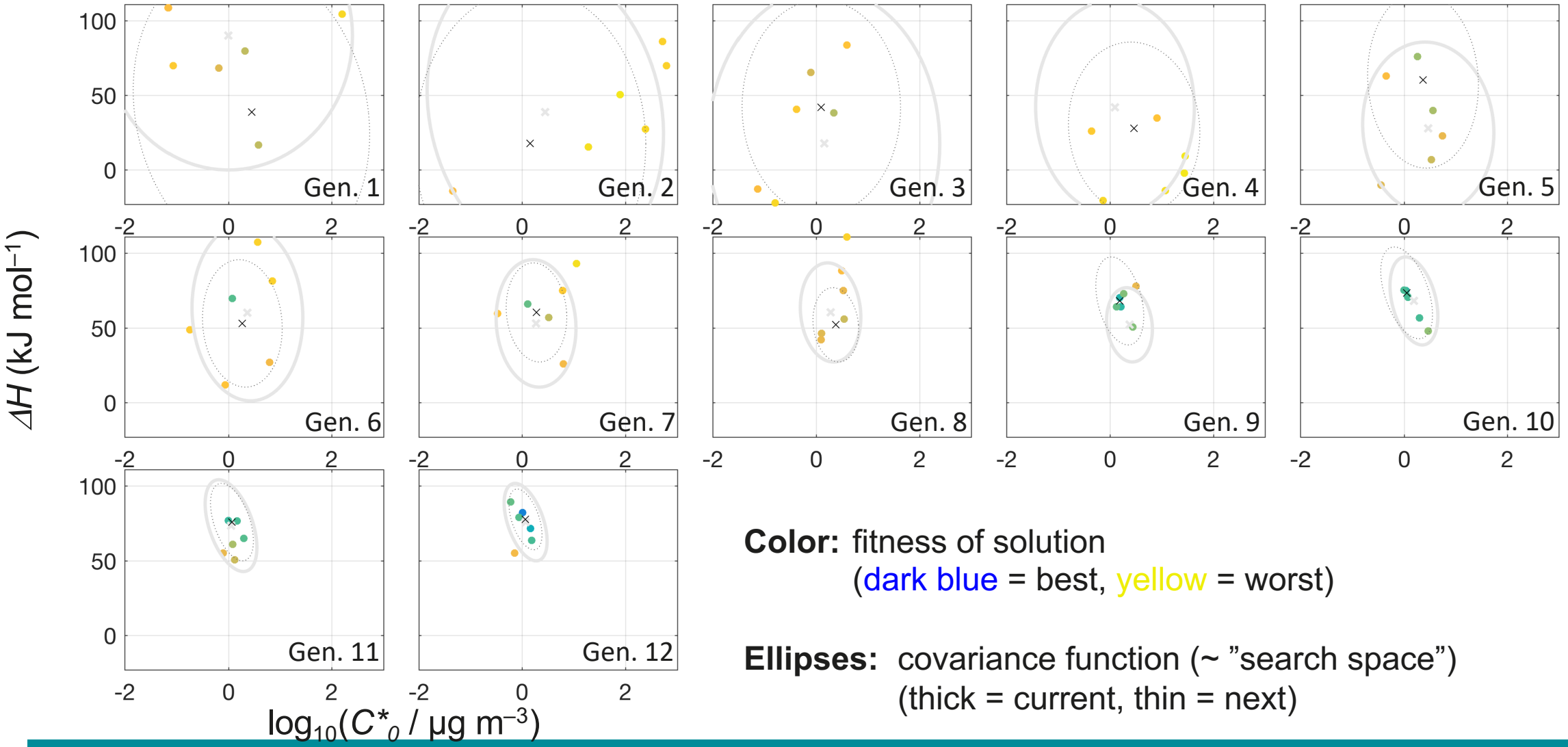
WHY:

- Flexible regarding topography of objective function (not really required to be known)
- Seems to be performing quite well overall
- Core MATLAB code can be copy-pasted from Wikipedia ☺

Automatic thermogram fitting: **CMA-ES as optimizer**

E.g., cluster #2 initial slope fitting (2 free parameters):

Computing time: 4 min
(2013 MacBookPro, 3.1 GHz Core i7, 16 GB 1.9 GHz DDR3)



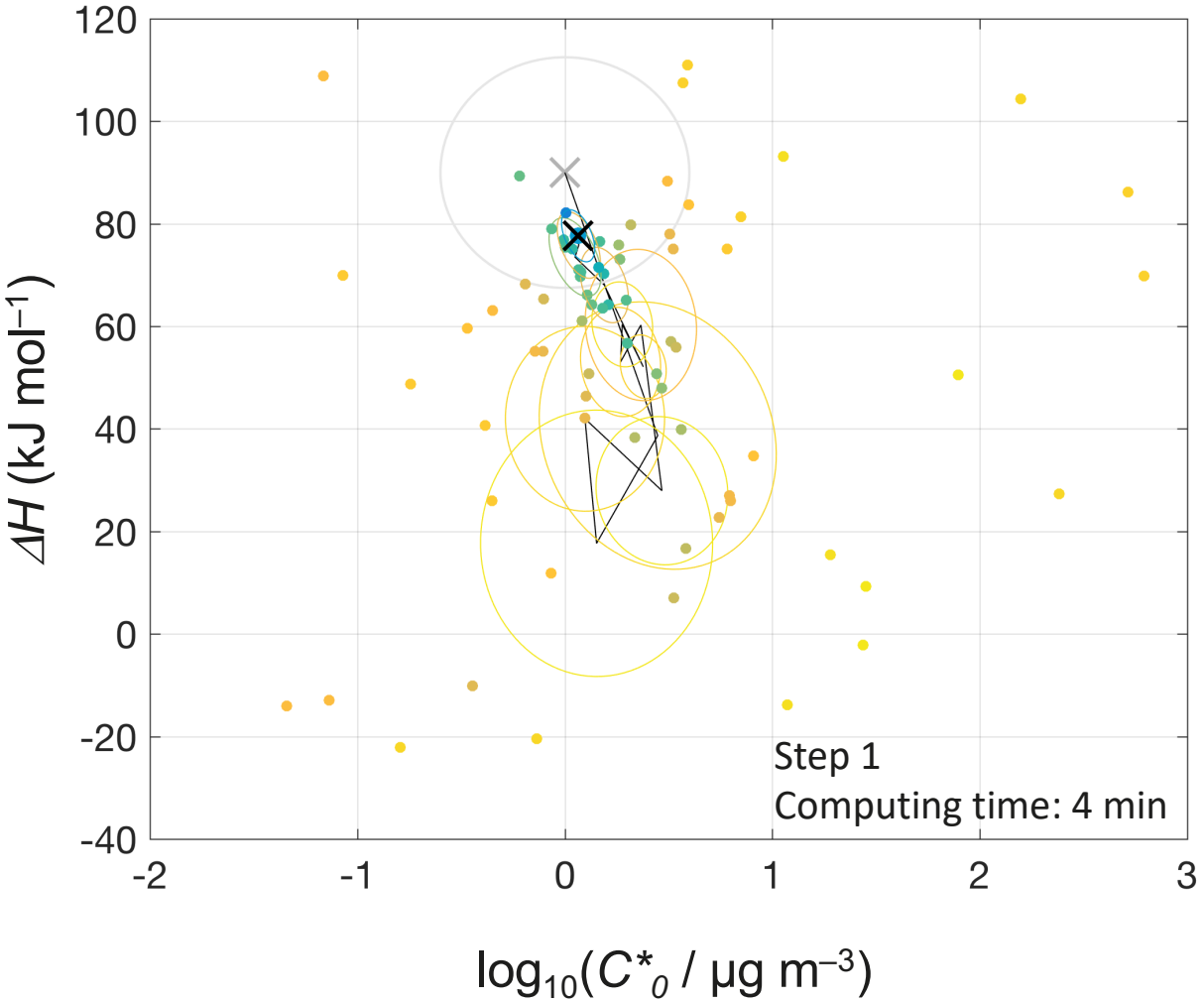
Color: fitness of solution
(dark blue = best, yellow = worst)

Ellipses: covariance function (~ ”search space”)
(thick = current, thin = next)

Automatic thermogram fitting: **CMA-ES as optimizer**

E.g., cluster #2 initial slope fitting.

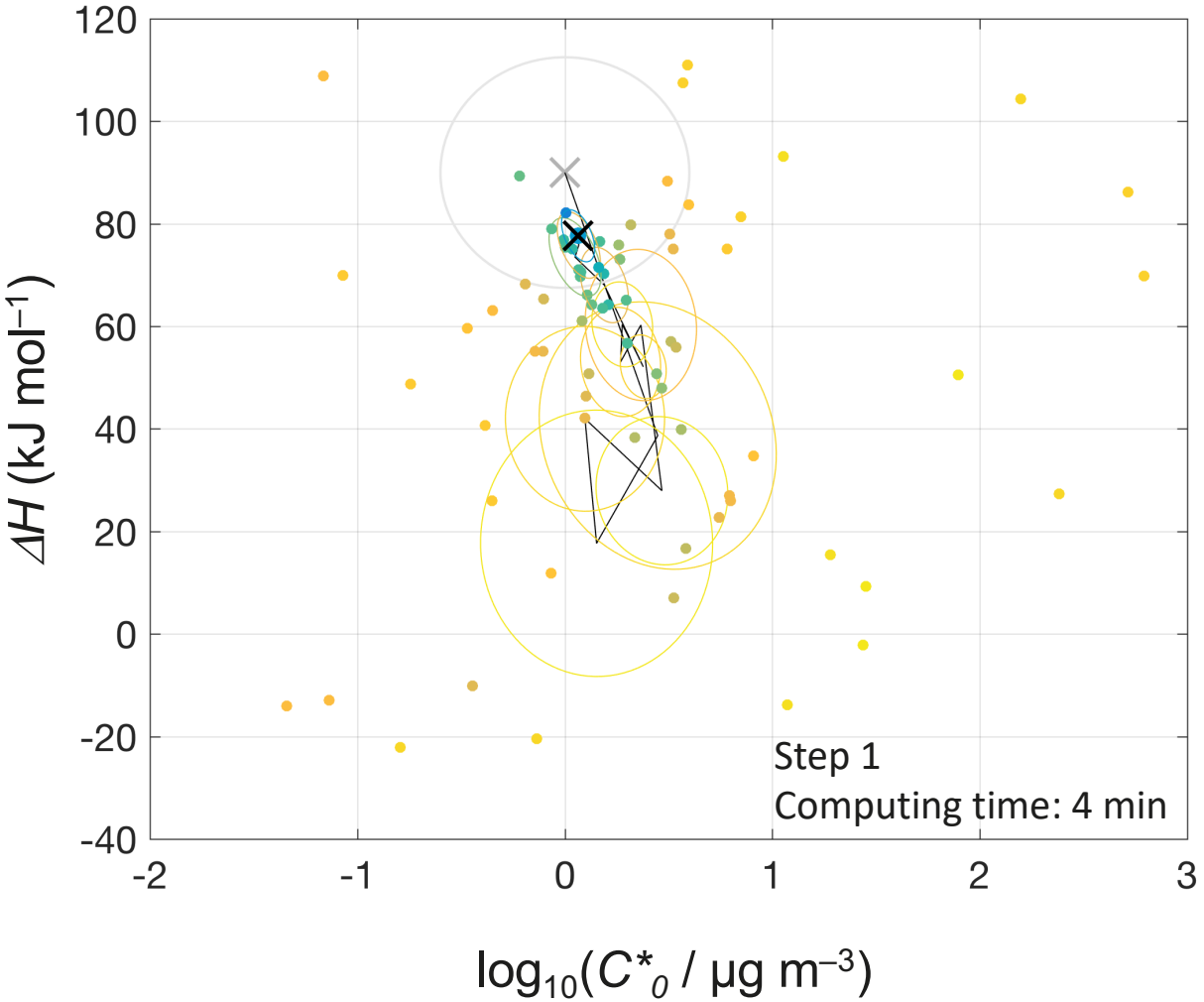
All in one plot:



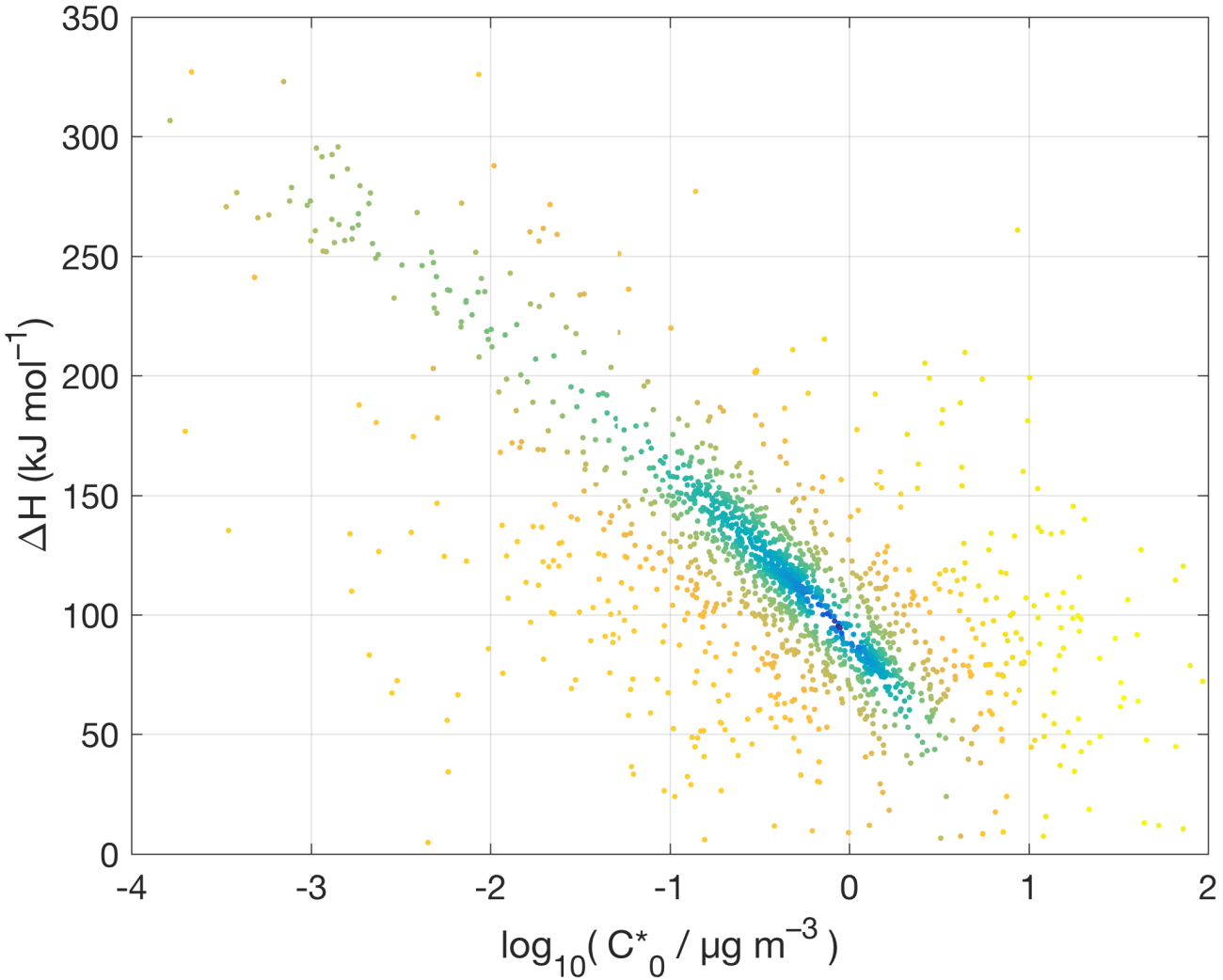
Automatic thermogram fitting: **CMA-ES as optimizer**

E.g., cluster #2 initial slope fitting.

All in one plot:



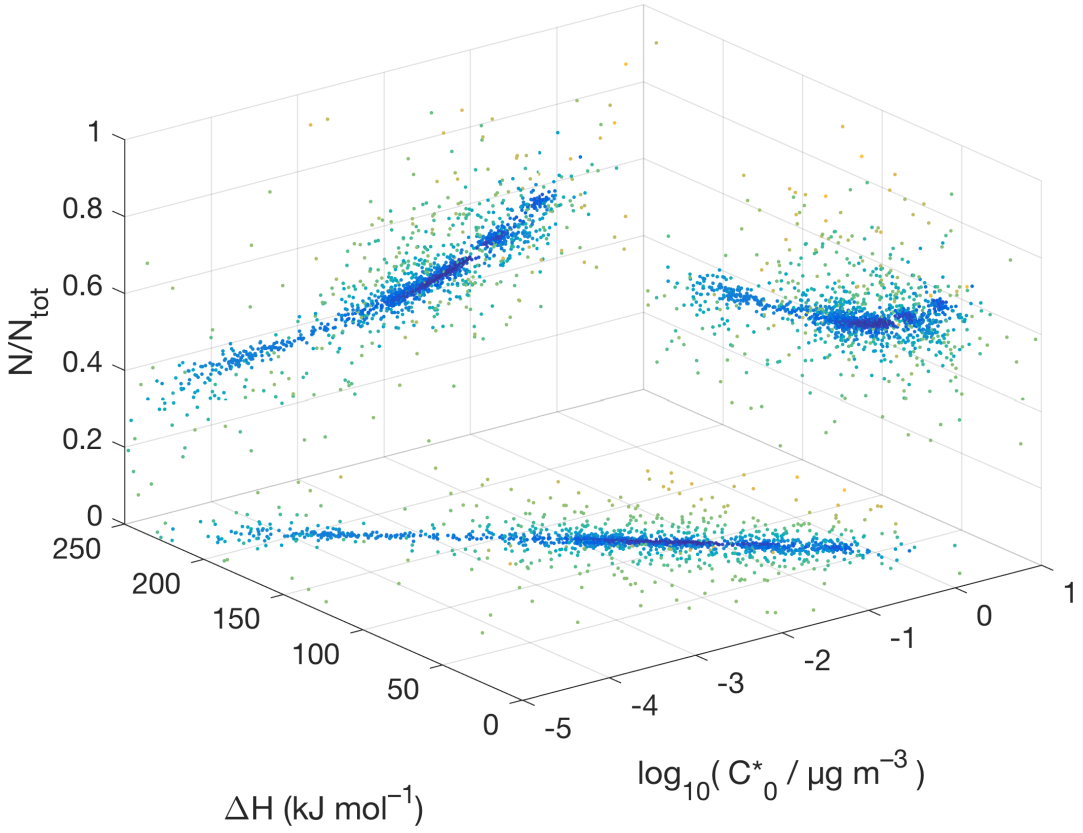
1668 runs to explore objective function (cluster #3 actually):



Automatic thermogram fitting: **CMA-ES as optimizer**

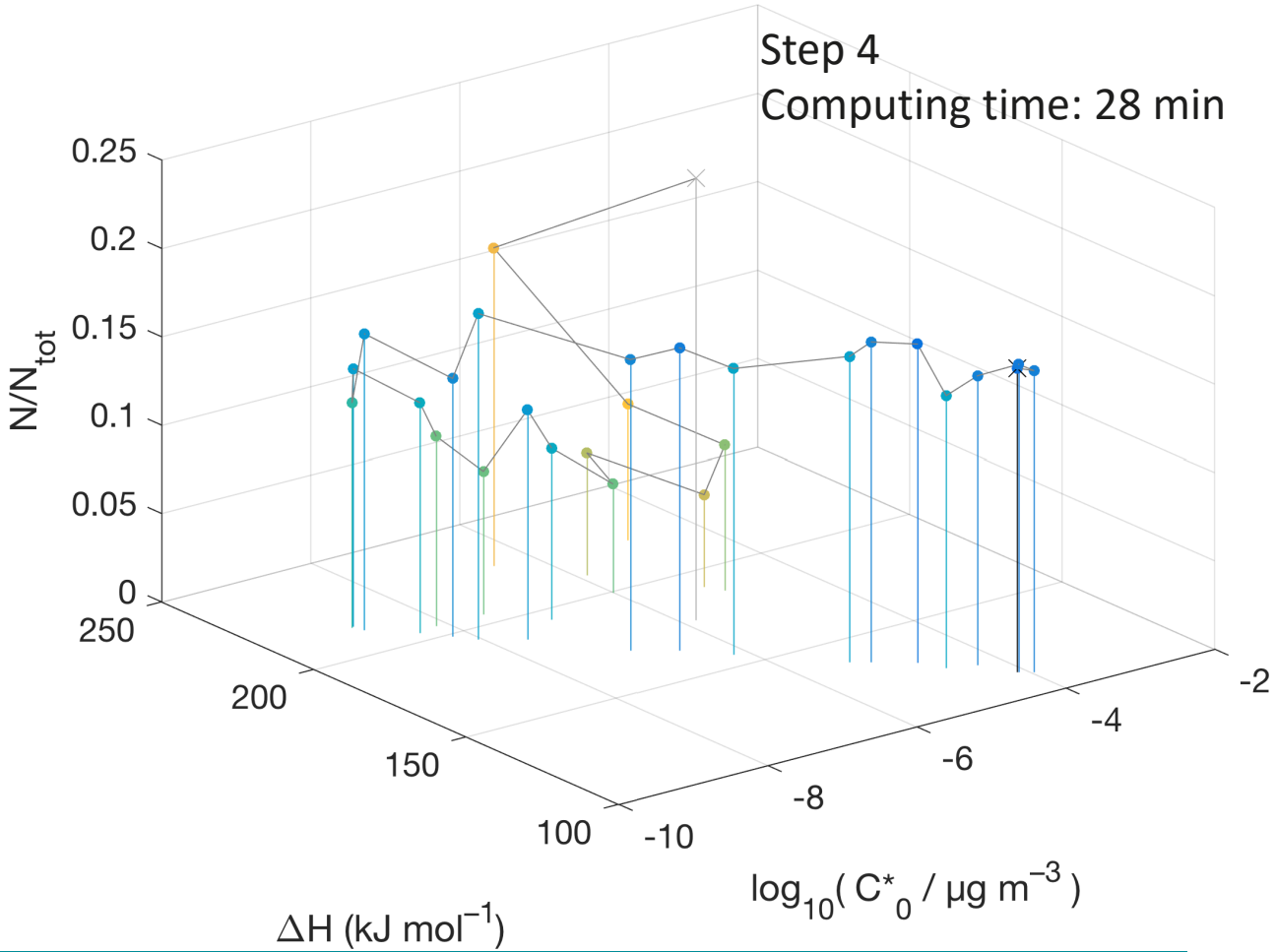
Step 2 (3 parameters)

Example topography of objective function:



E.g., "wandering off" but making U-turn:

Here only showing **mean results** for each generation



Automatic thermogram fitting: **CMA-ES as optimizer**

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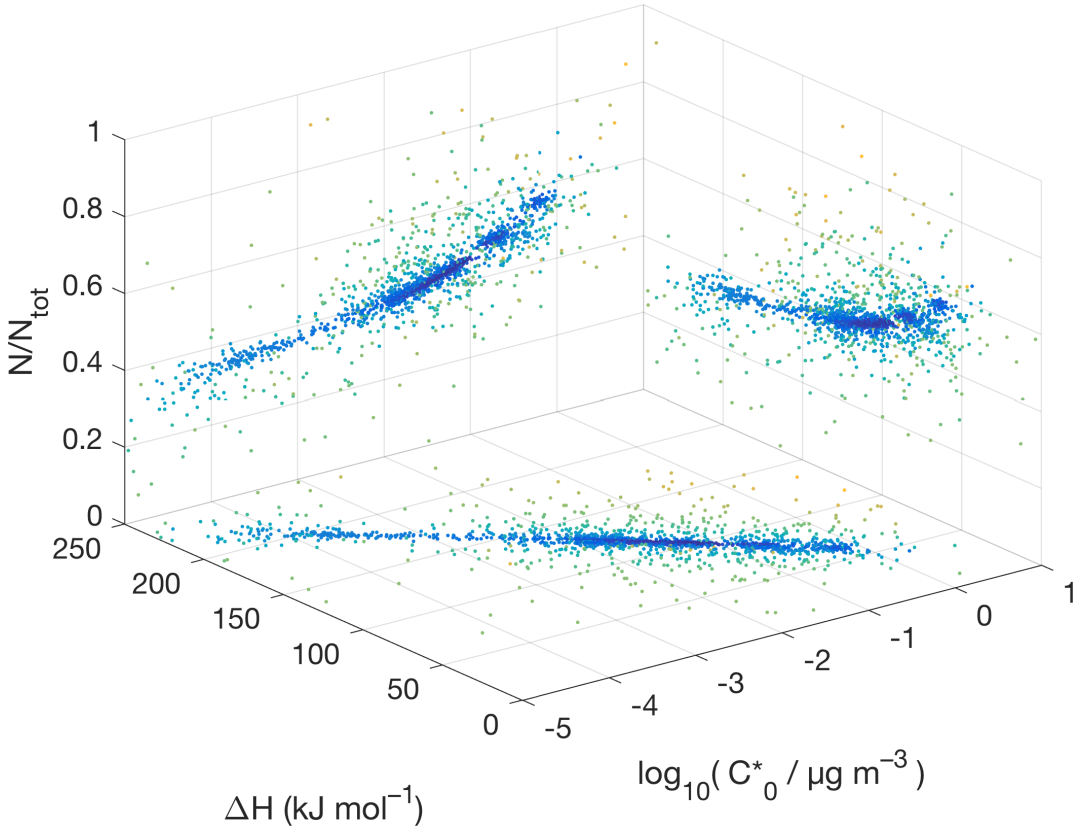

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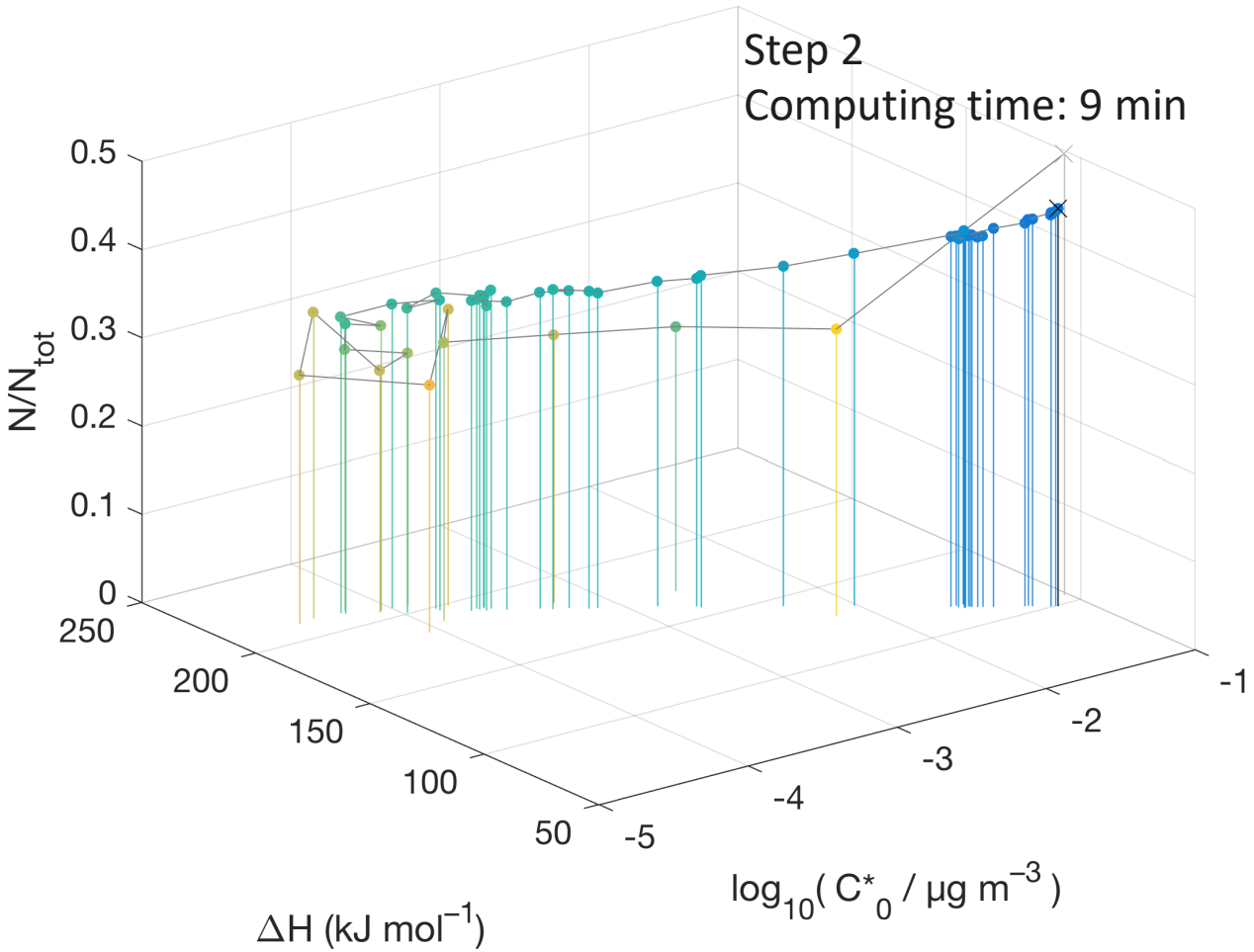
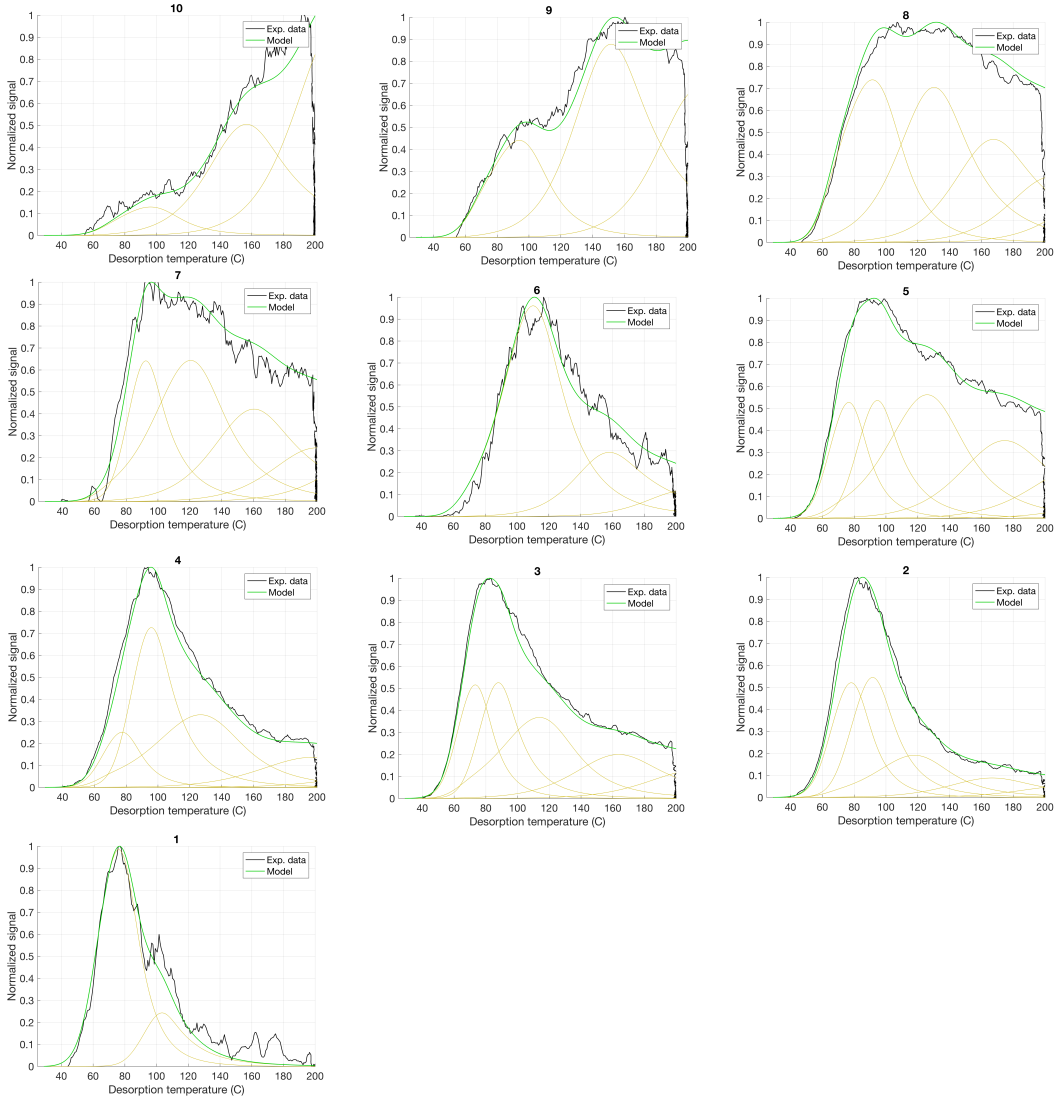


Automatic fitting probably not as good as “manual expert” fitting, but probably close enough (and less biased!?

Manual ”expert” fitting results:



Automatic fitting results:

#10 *got lost*

52 min

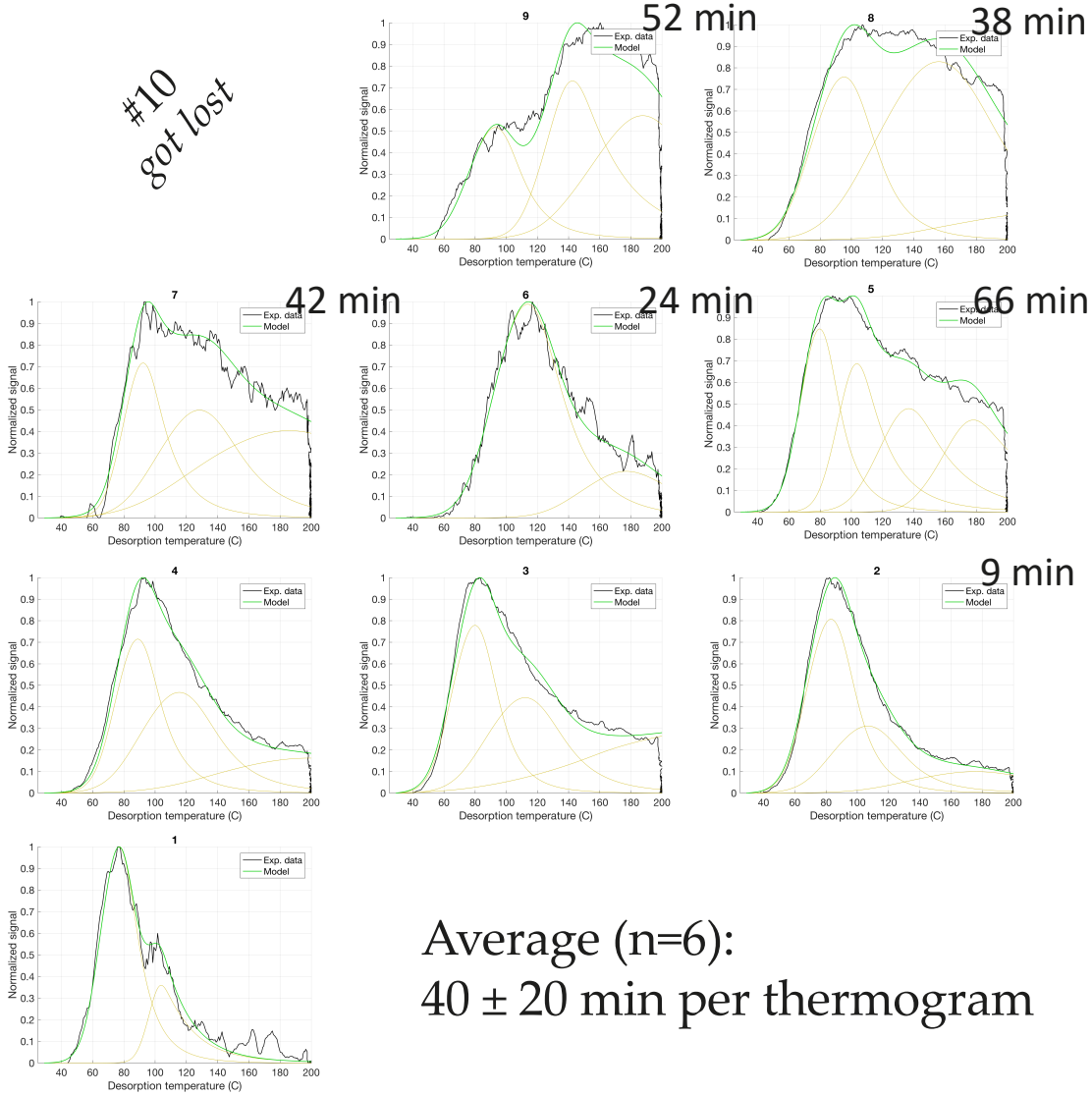
38 min

42 min

24 min

66 min

9 min

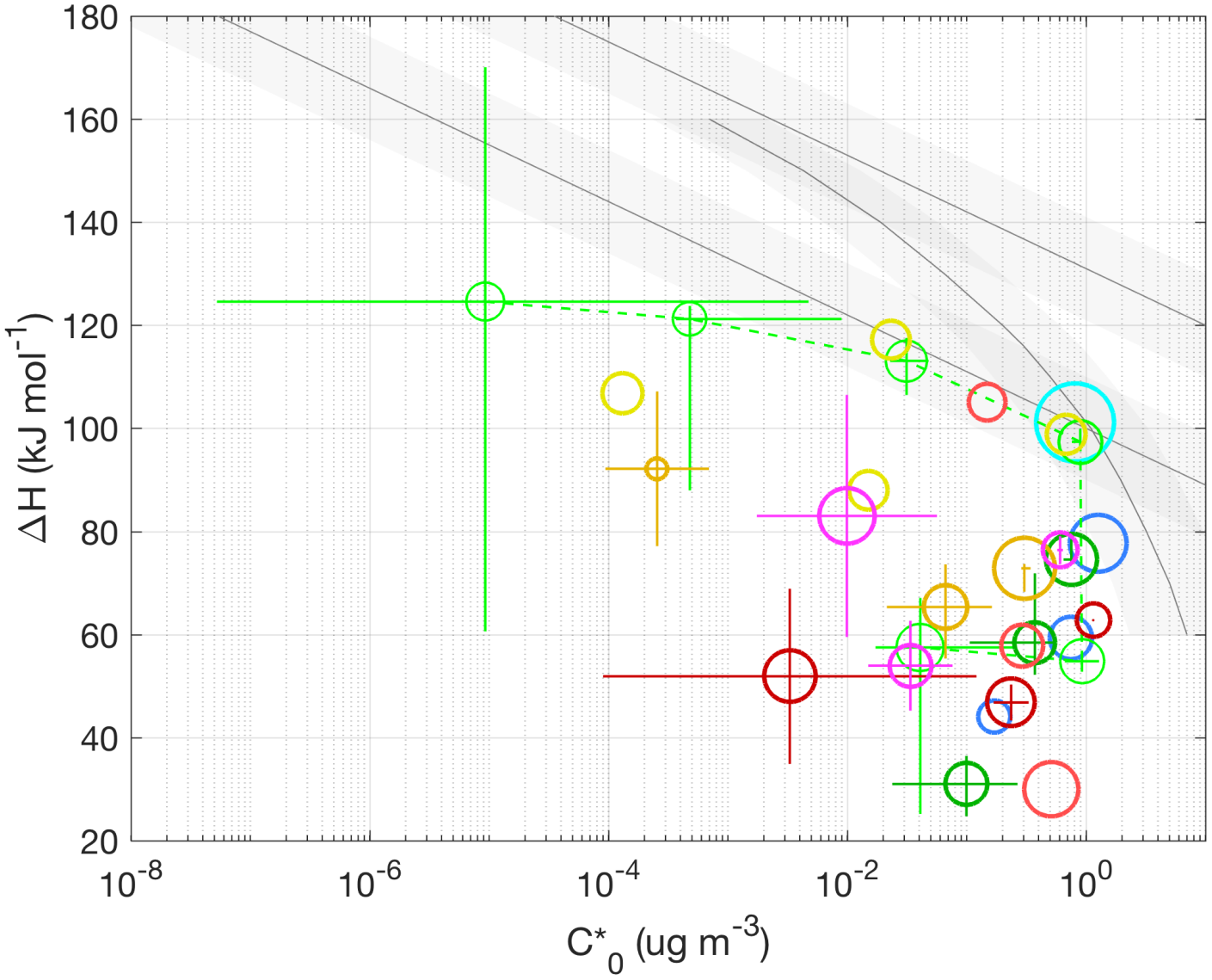


Average (n=6):
40 ± 20 min per thermogram

Summing up the results:

Multiple runs for some clusters: # 1,2, 7, 5: 1 run
8, 9: 2 runs
6: 4 runs
3, 4: 6 runs

Abundances:



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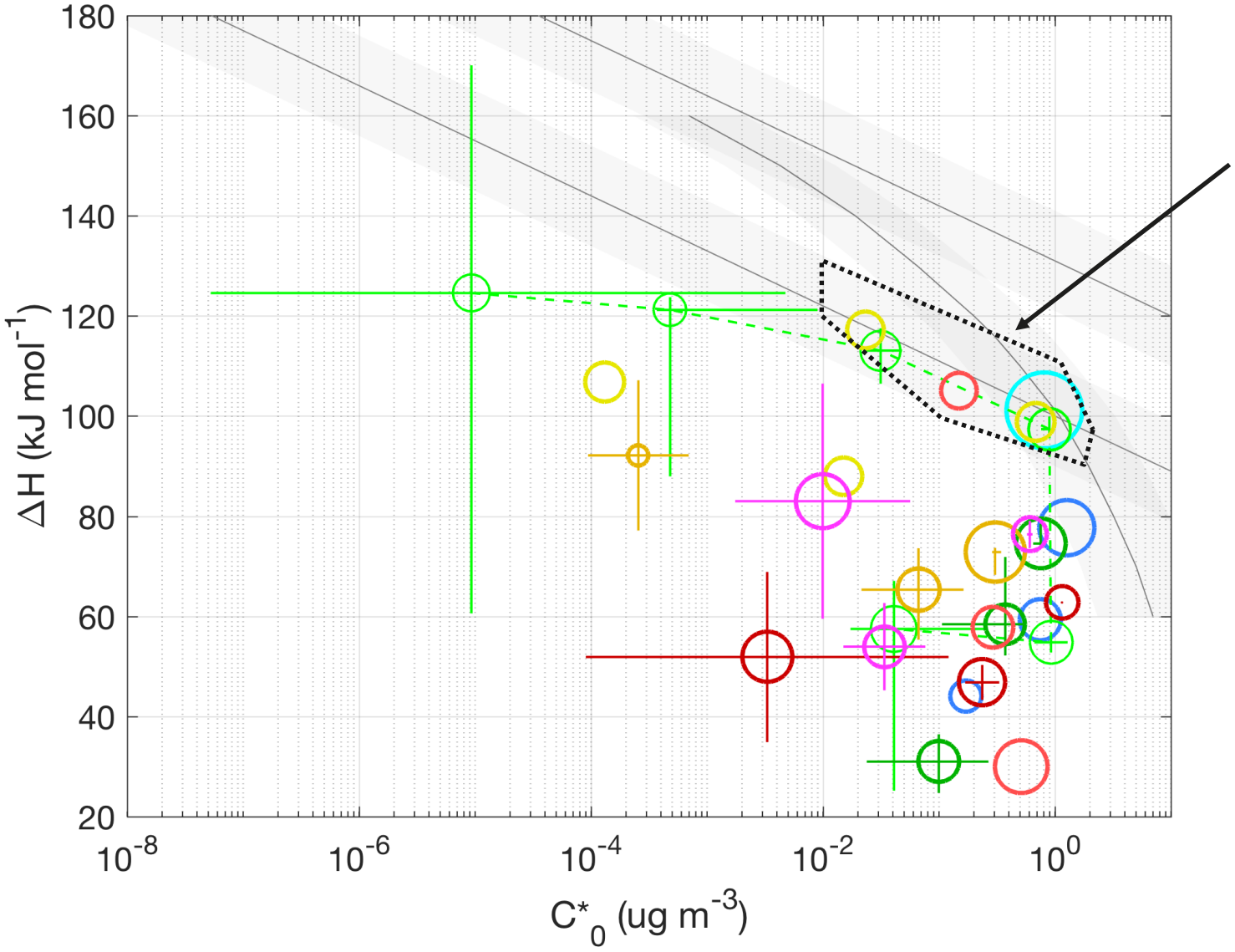

"Free monomer" region from manual fitting

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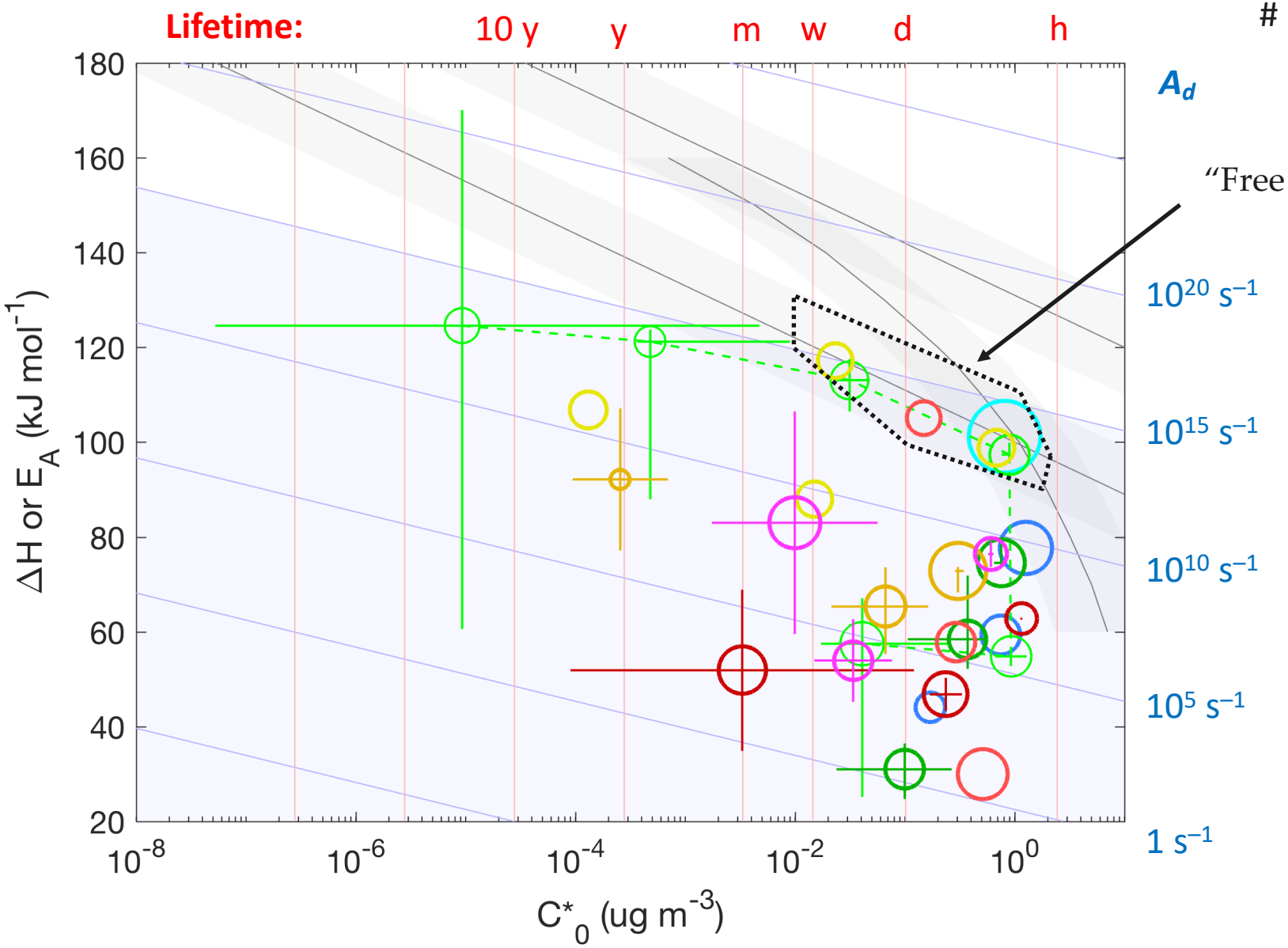

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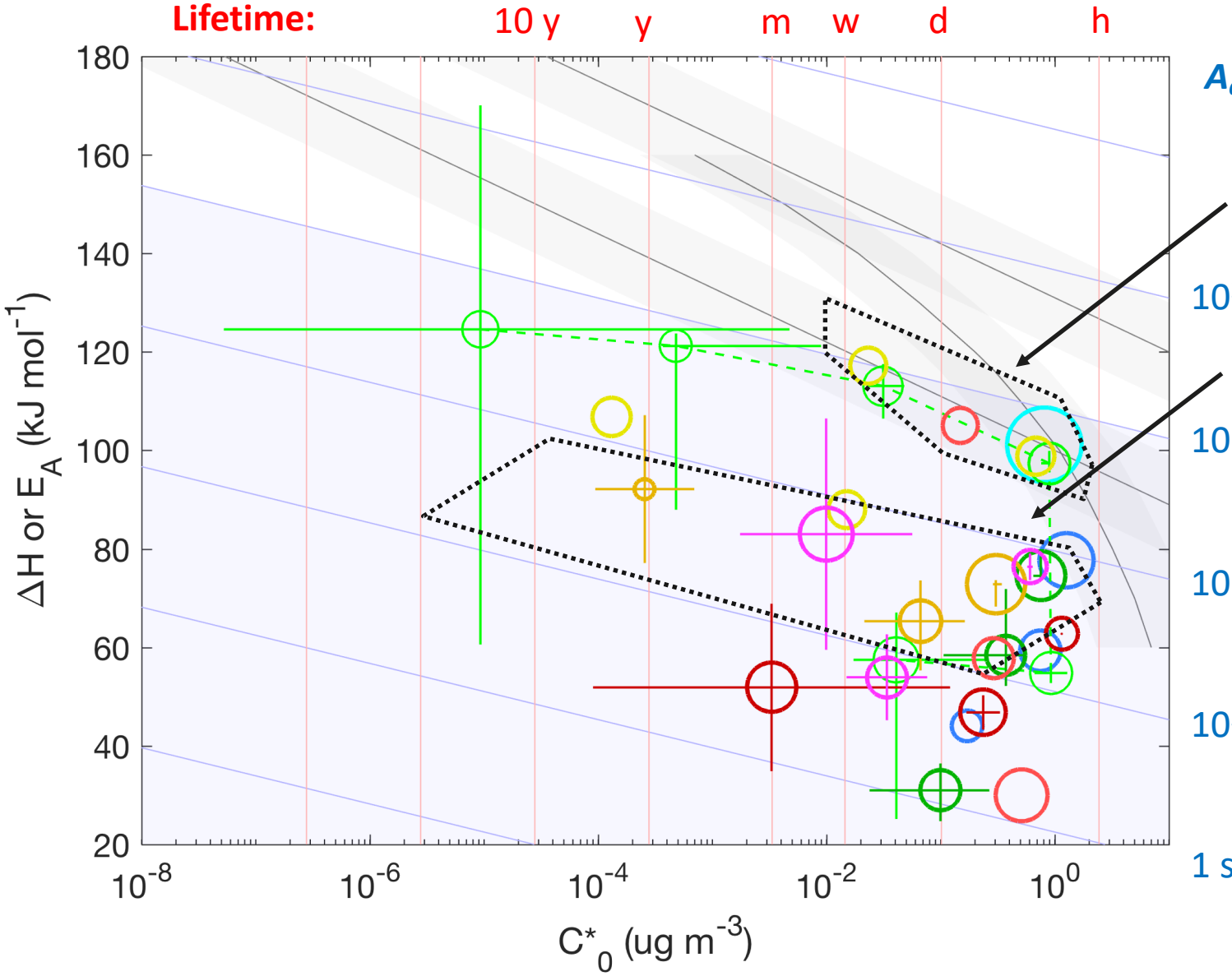


A_d

10^{20} s^{-1}

10^{15} s^{-1}

10^{10} s^{-1}

10^{5} s^{-1}

1 s^{-1}

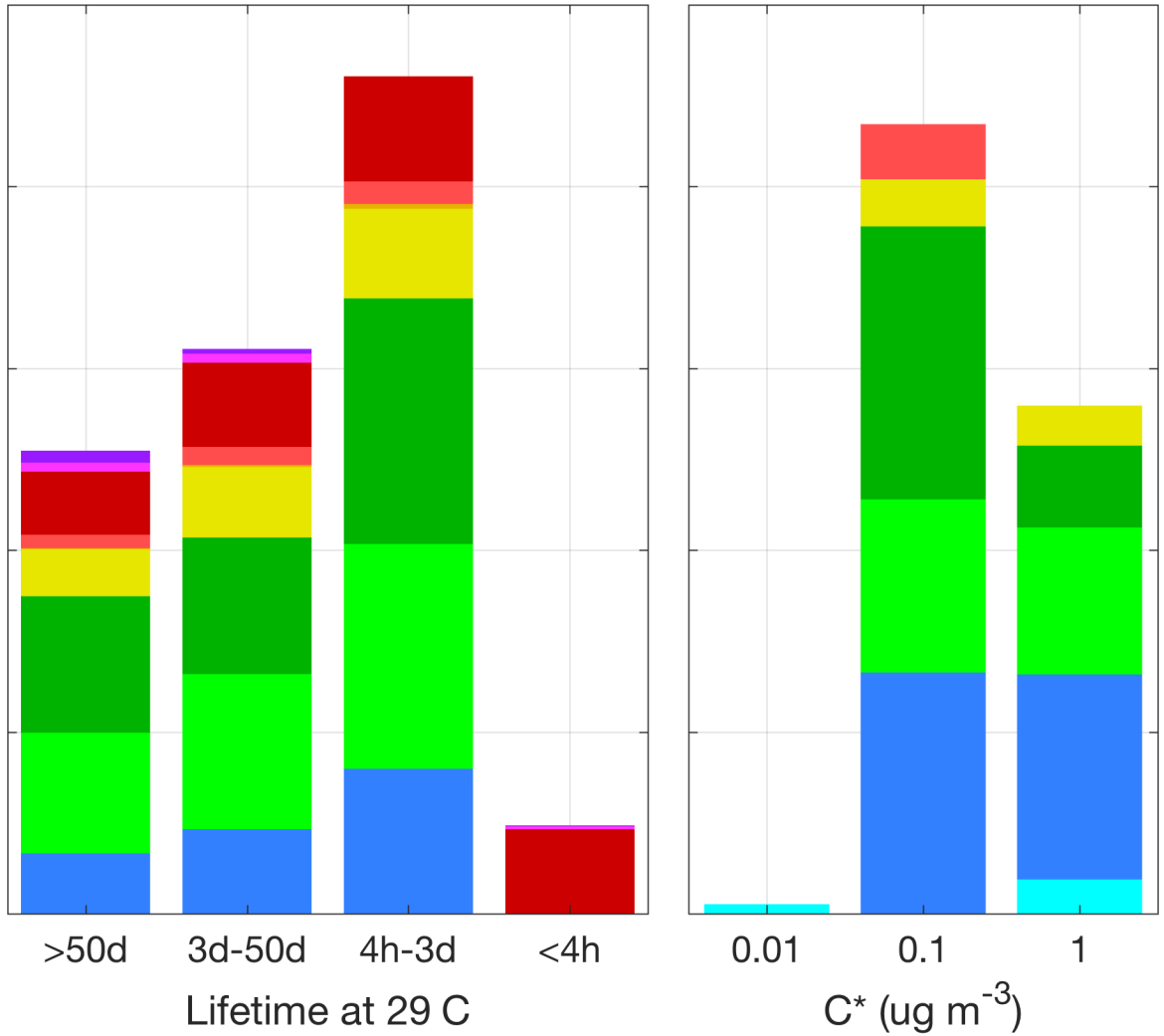
"Free monomer" region from manual fitting

Decomposition region from manual fitting

[Should I constrain A_d when fitting for getting more unique solutions?]

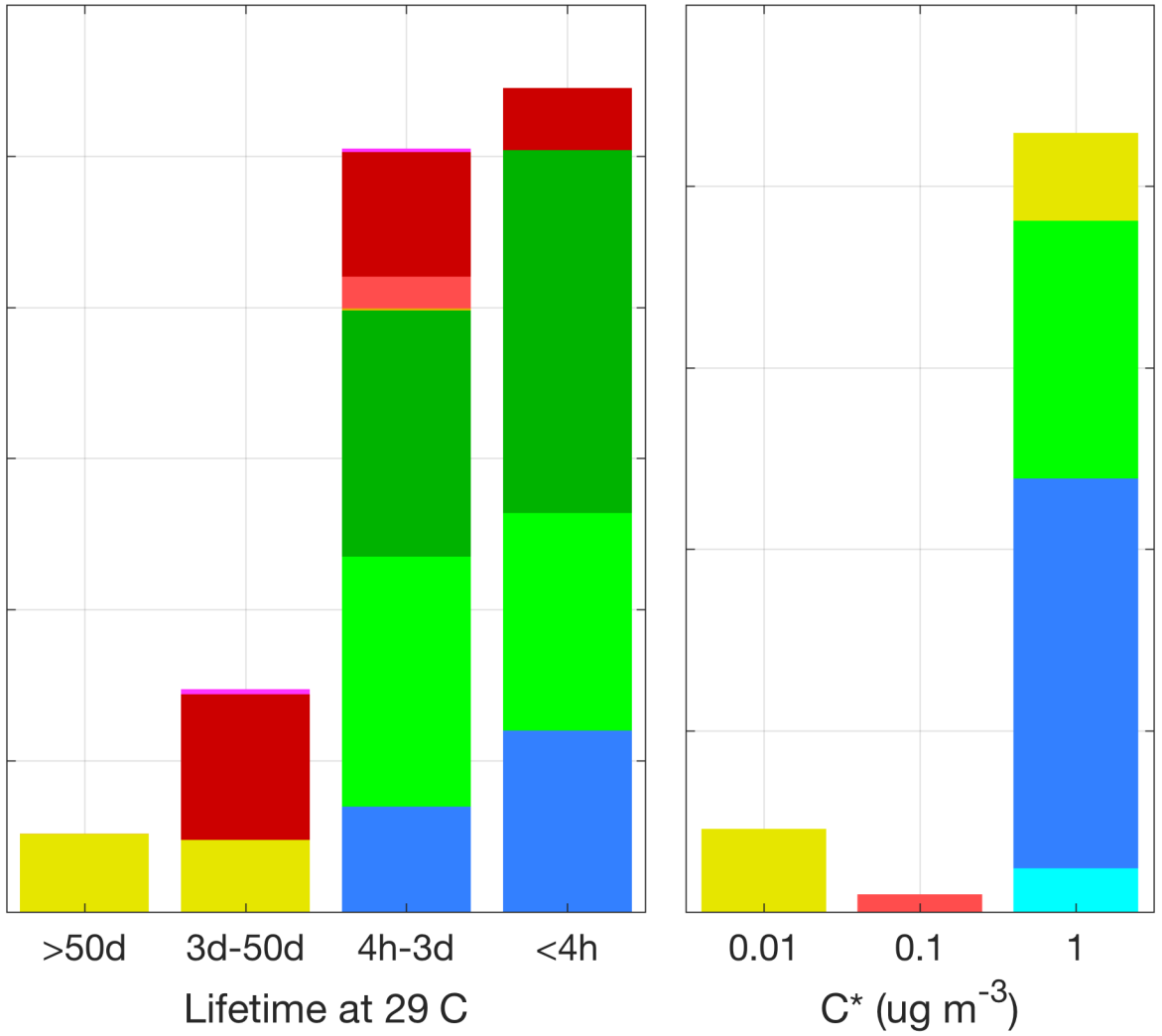
Summing up the results → VBS-style plot

Manual:



vs.

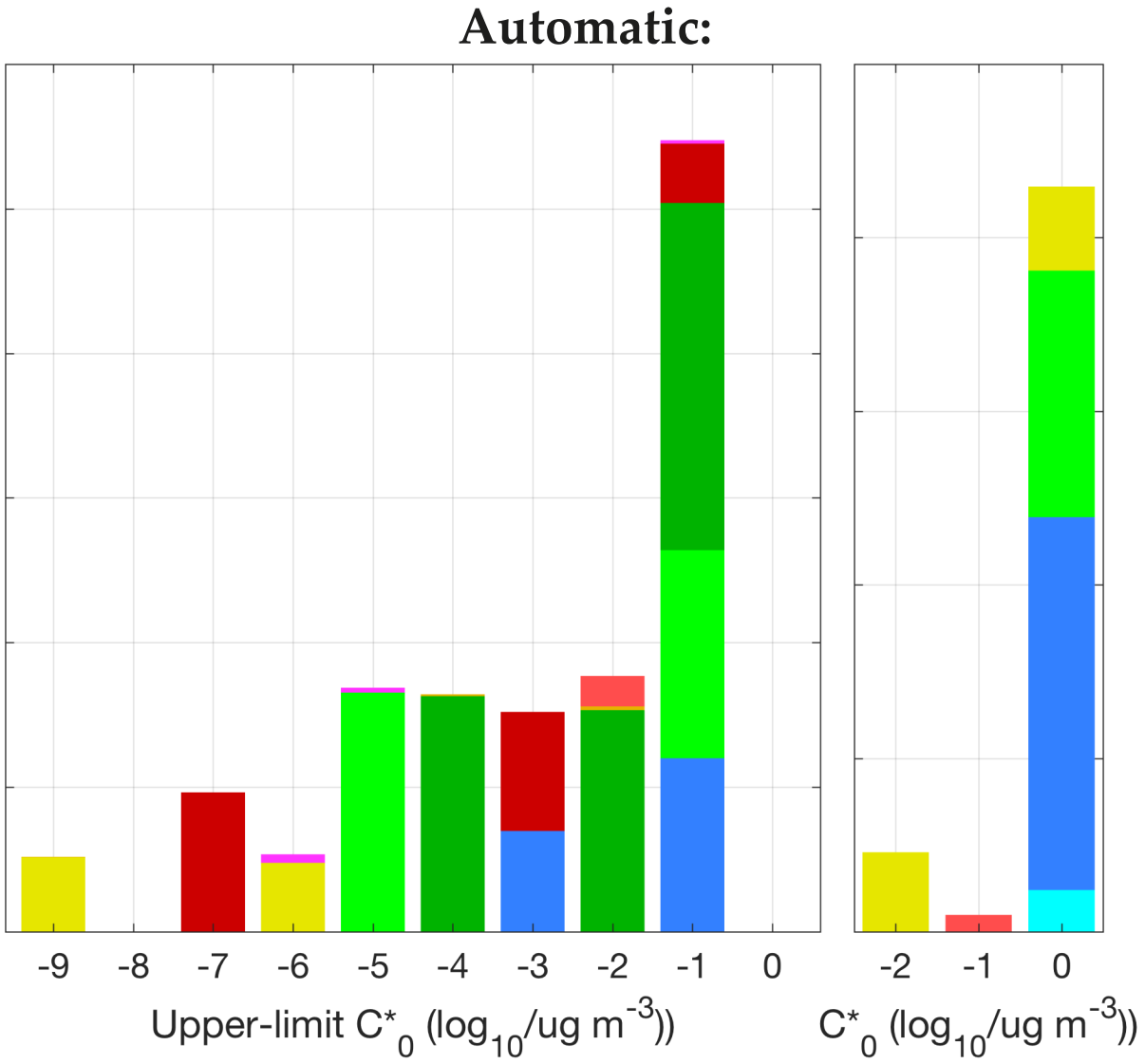
Automatic:



Summing up the results → VBS-style plot

If C^*_0-ΔH relationship is assumed known:

Can covert from decomposition lifetimes rough **upper-limit C^*_0 values** for the parent compounds (if higher, the compounds would rather evaporate than decompose).



Conclusions:

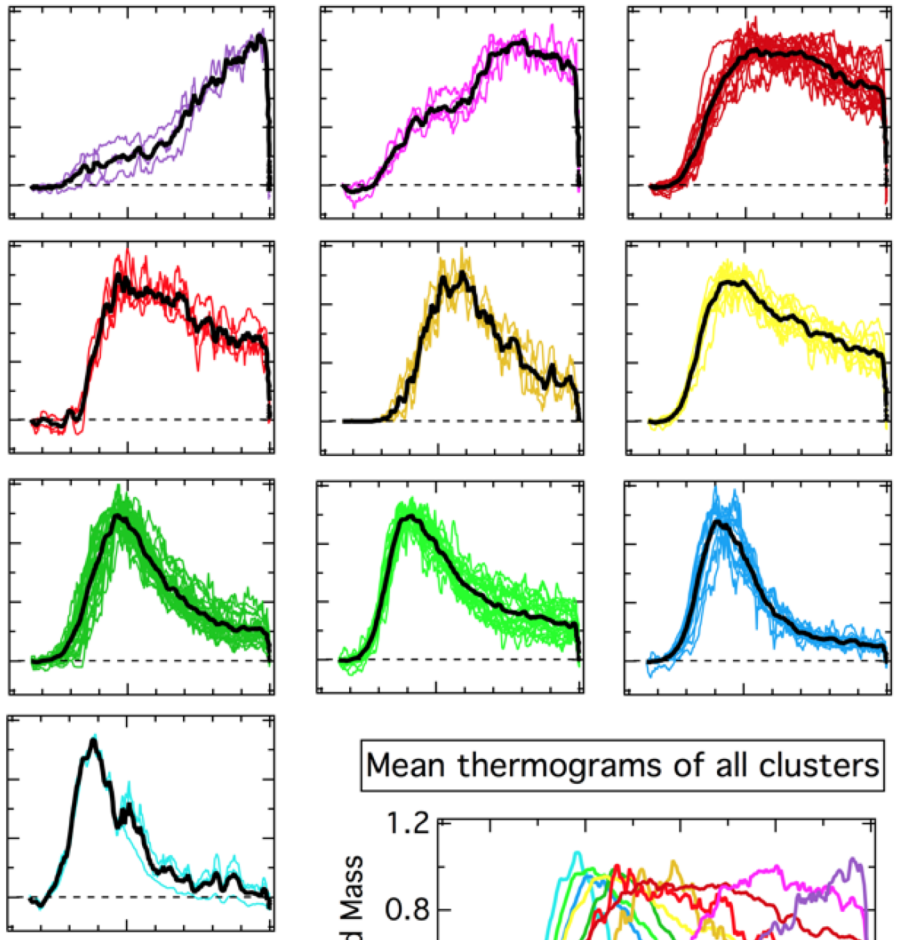
- Automatic fitting routine gives **sensible solutions**, in general, but **not always unique.**
- It is fast enough to fit dozens of thermograms per day (on my computer).
- Additional experimental results could add constraints on fitting parameters => more accurate results.

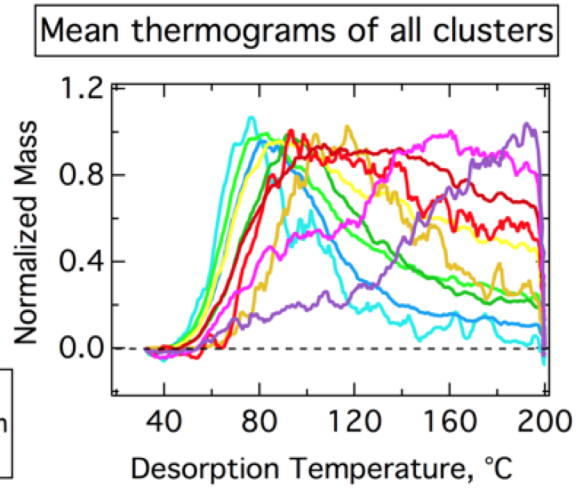
Future work:

- Try to only allow **certain range of A_d?**
- Try better estimates of "goodness" of fit? (currently minimizing ordinary least squares)
- Some work on **quantifying "goodness"** of fit for multi-peak fitting would speed things up!
- Could optimize **peak/slope range localization routine** (thermograms ≠ mass spectrum!)
- More suitable optimization routine than CMA-ES? Or could parameters be set better?
- Extend to allow inclusion of isothermal evaporation periods (cf. D'Ambro et al., ACS ESC, 2018)
- **Apply to datasets!**

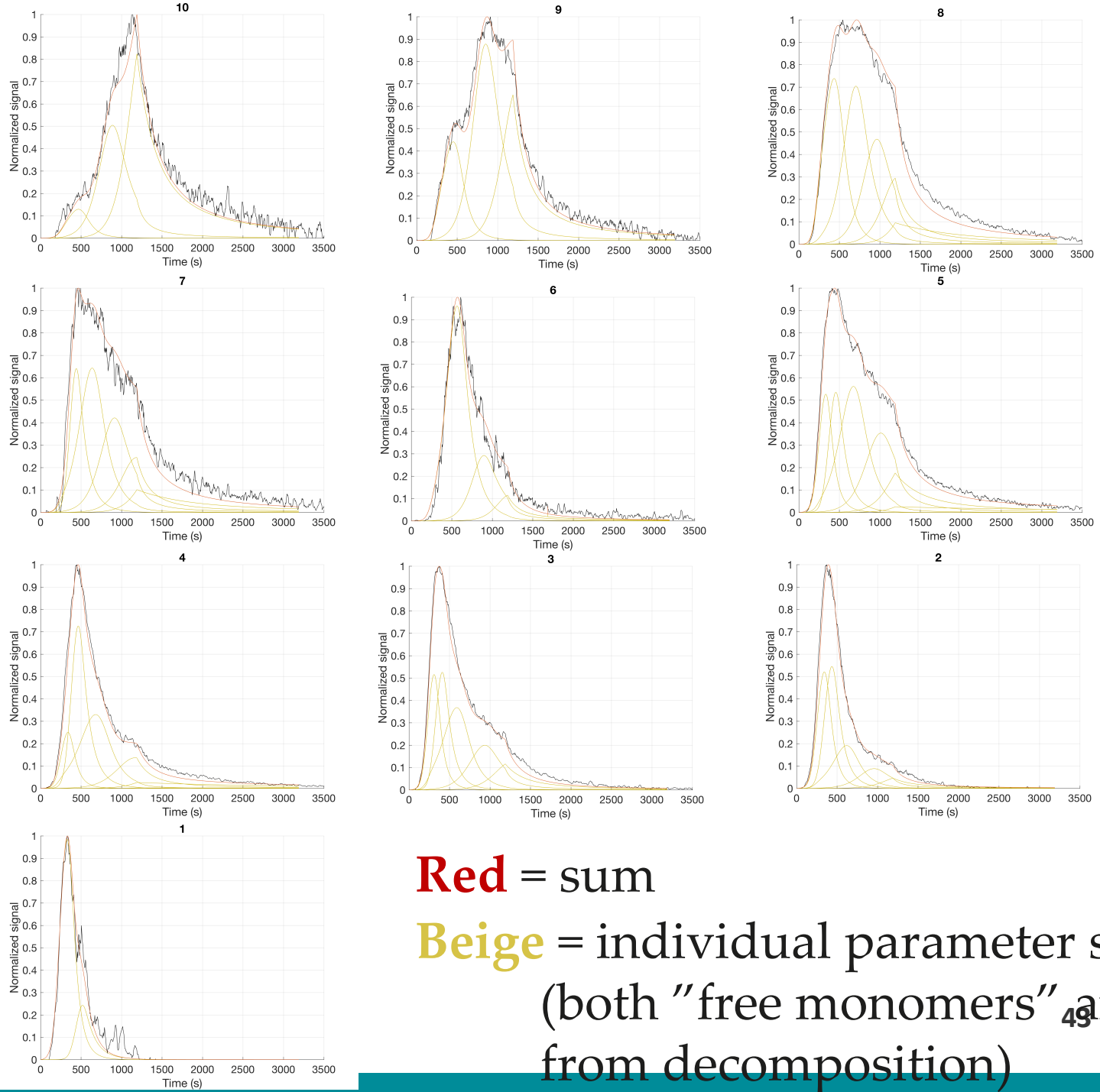
Backup slides

a-Pinene
Clusters 1-10





For each cluster
Individual thermogram
Mean thermogram



Red = sum

Beige = individual parameter sets (both "free monomers" and from decomposition)

Values of A (s^-1) I ended up using for now:
cluster 1: n/a
cluster 2: 1.1e7
cluster 3: 7e6
cluster 4: 5e5 (that’s the lowest)
cluster 5: 1e7
cluster 6: 3e11 (that’s the highest)
cluster 7: 5e7
cluster 8: 2e8
cluster 9: 5e8
cluster 10: 1.5e8

Efficient model-based retrieval of aerosol properties from composition-resolved thermal desorption measurements

Filter Inlet for Gas and AEROsol (FIGAERO)

Lopez-Hilfiker et al., AMT, 2014