UNIVERSITY OF CAMBRIDGE
Department of Chemistry

Assessing and improving the DMS oxidation mechanism in the MCM and CRI-Strat

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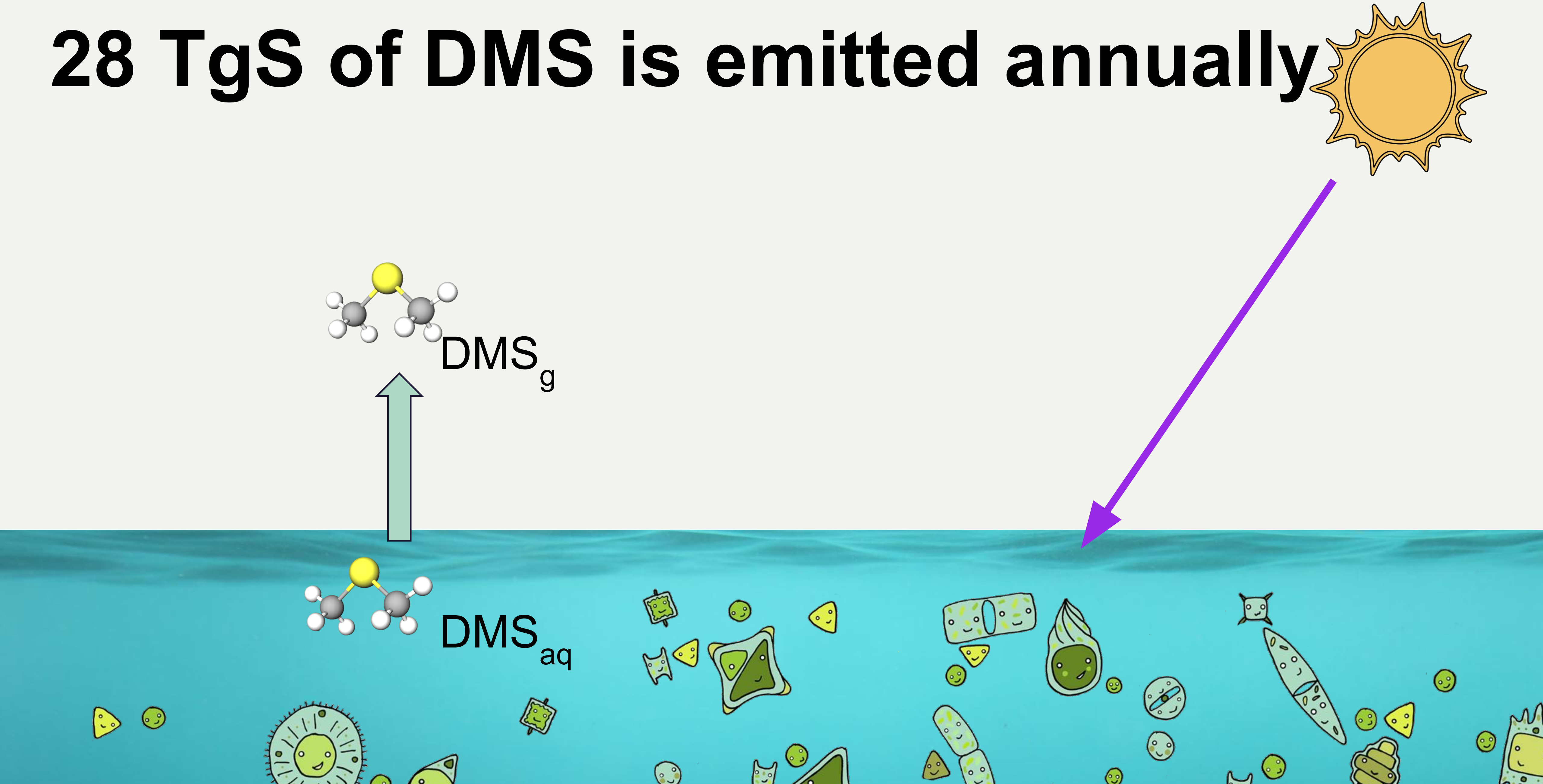
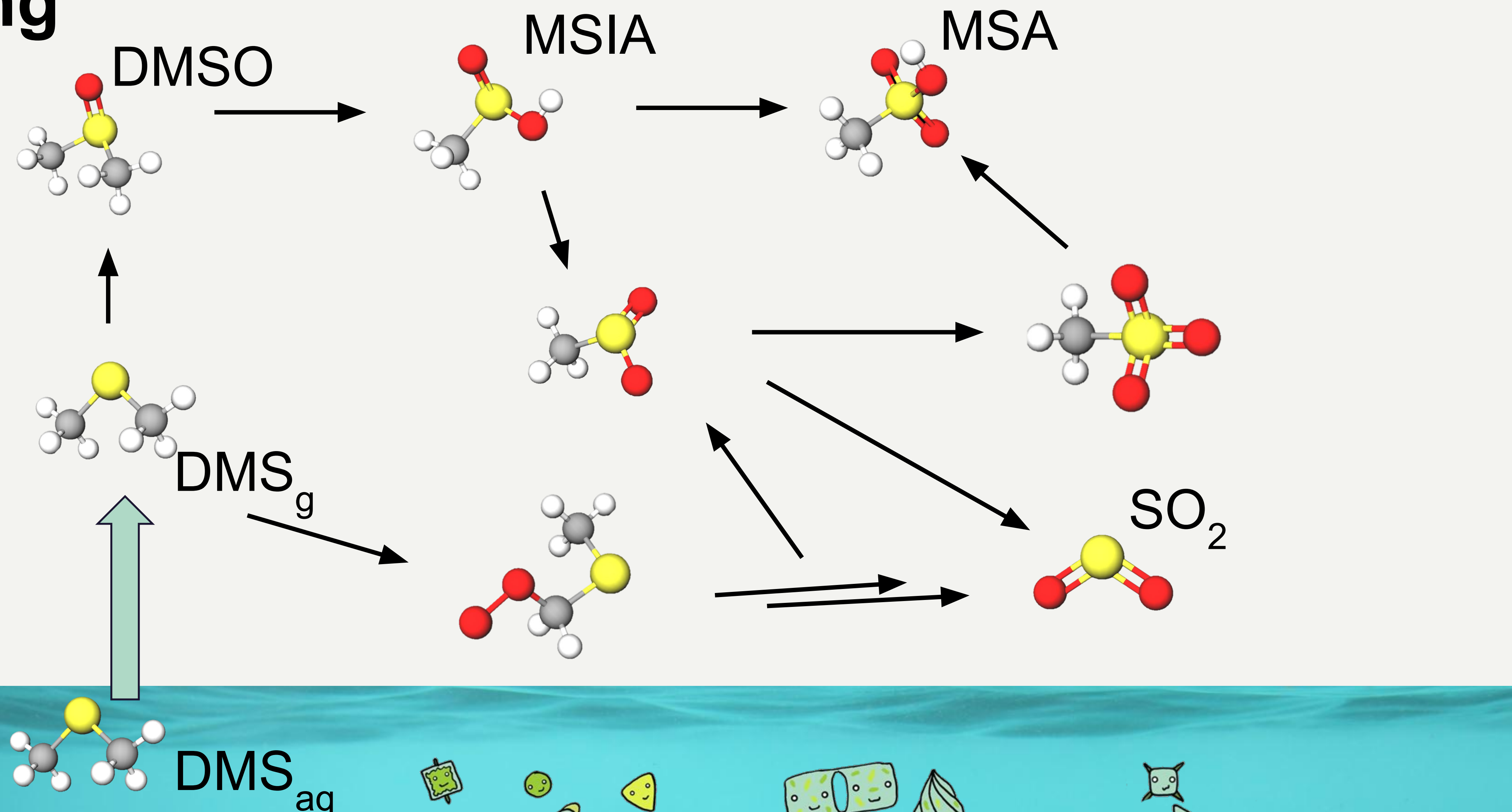
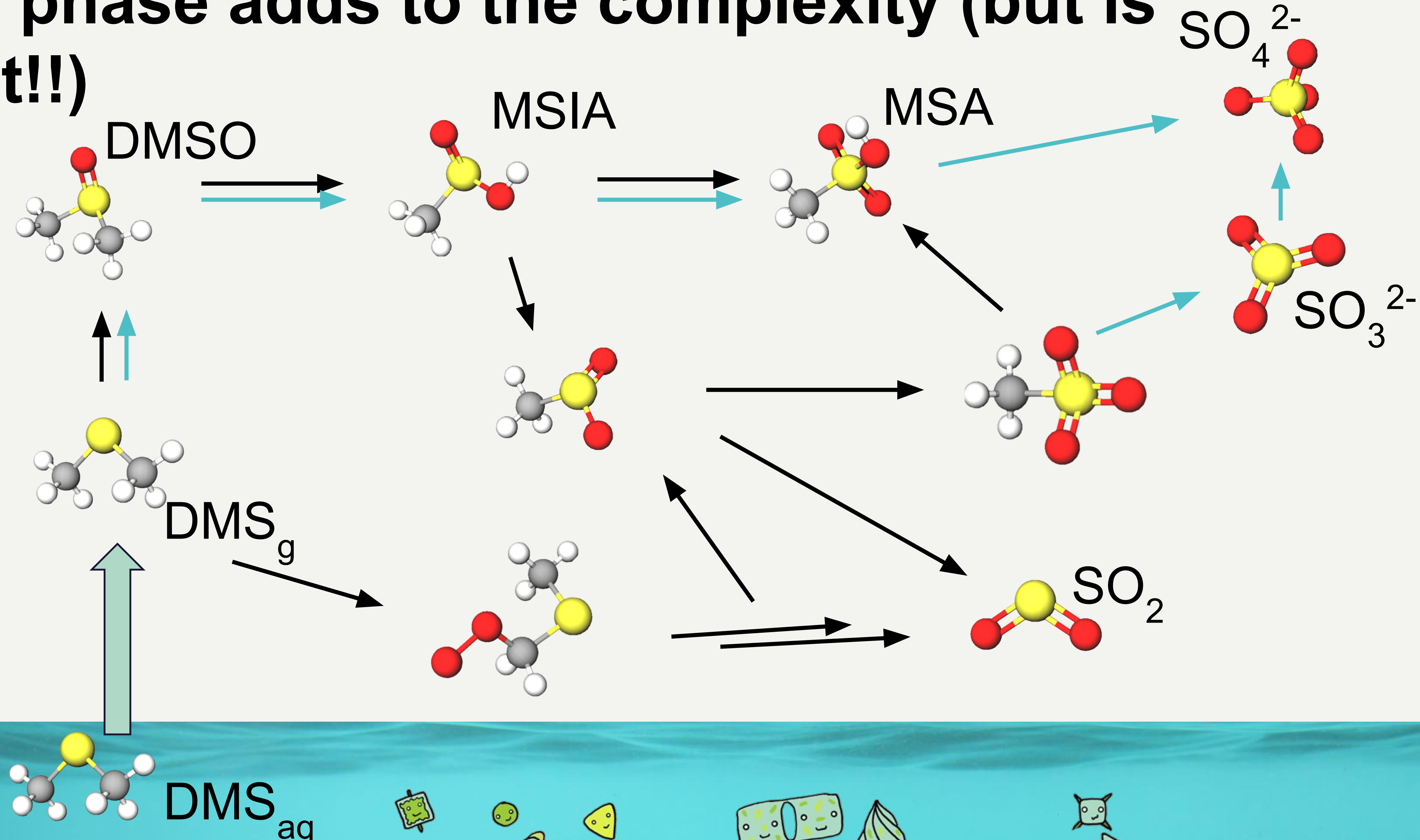
28 TgS of DMS is emitted annually



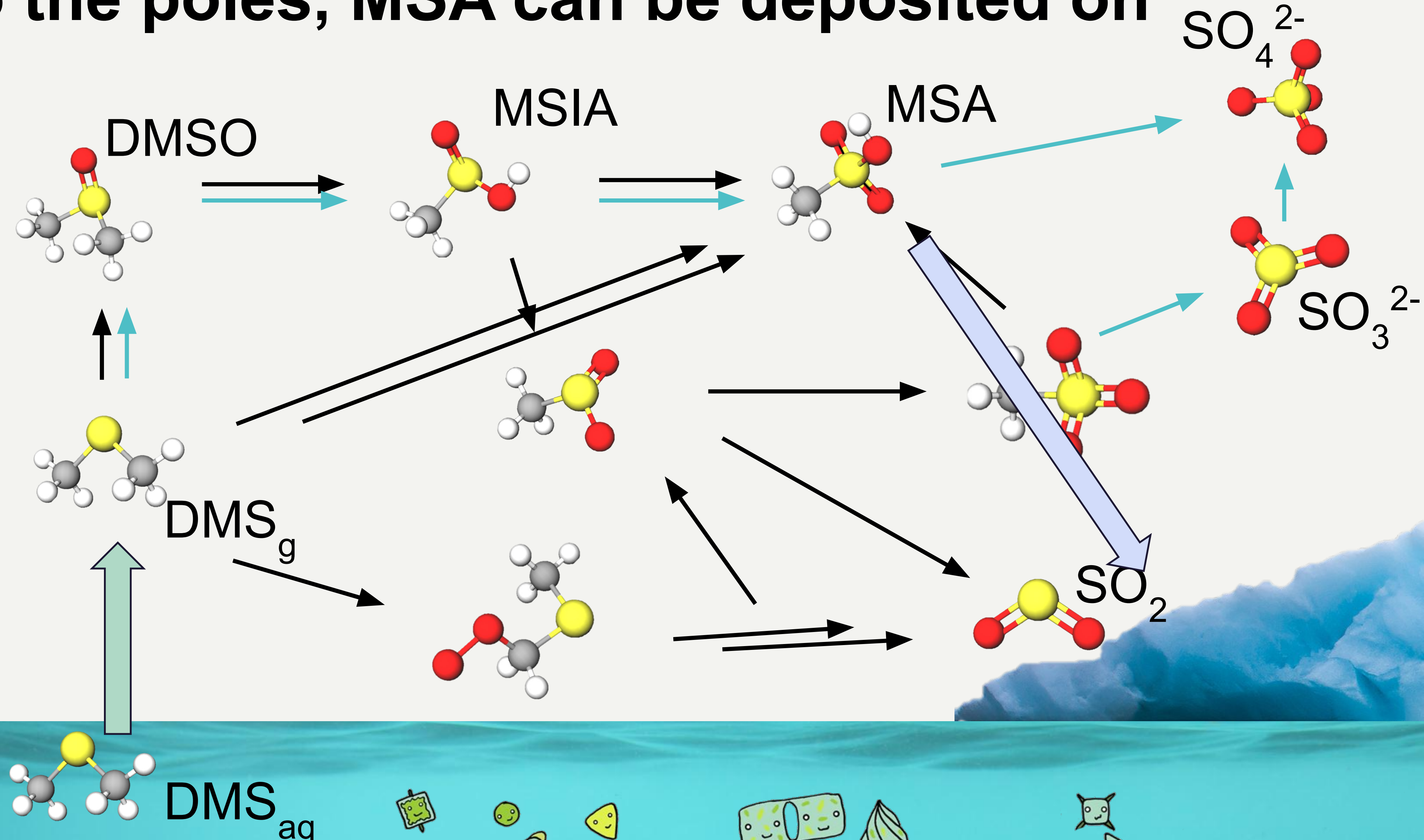
Once in the atmosphere, DMS chemistry gets interesting



Aqueous phase adds to the complexity (but is important!!)



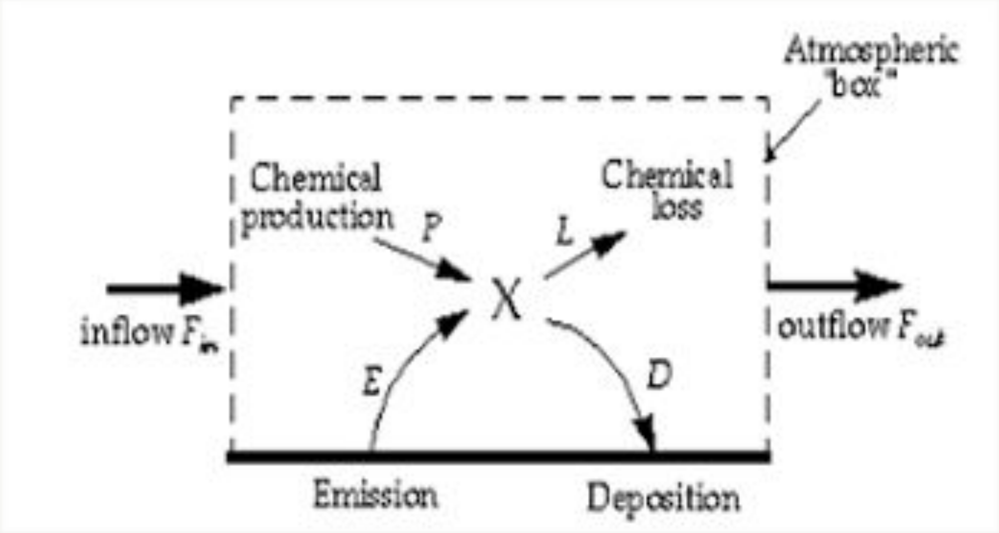
Closer to the poles, MSA can be deposited on ice



CRI-Strat and MCM are both useful, but have different uses

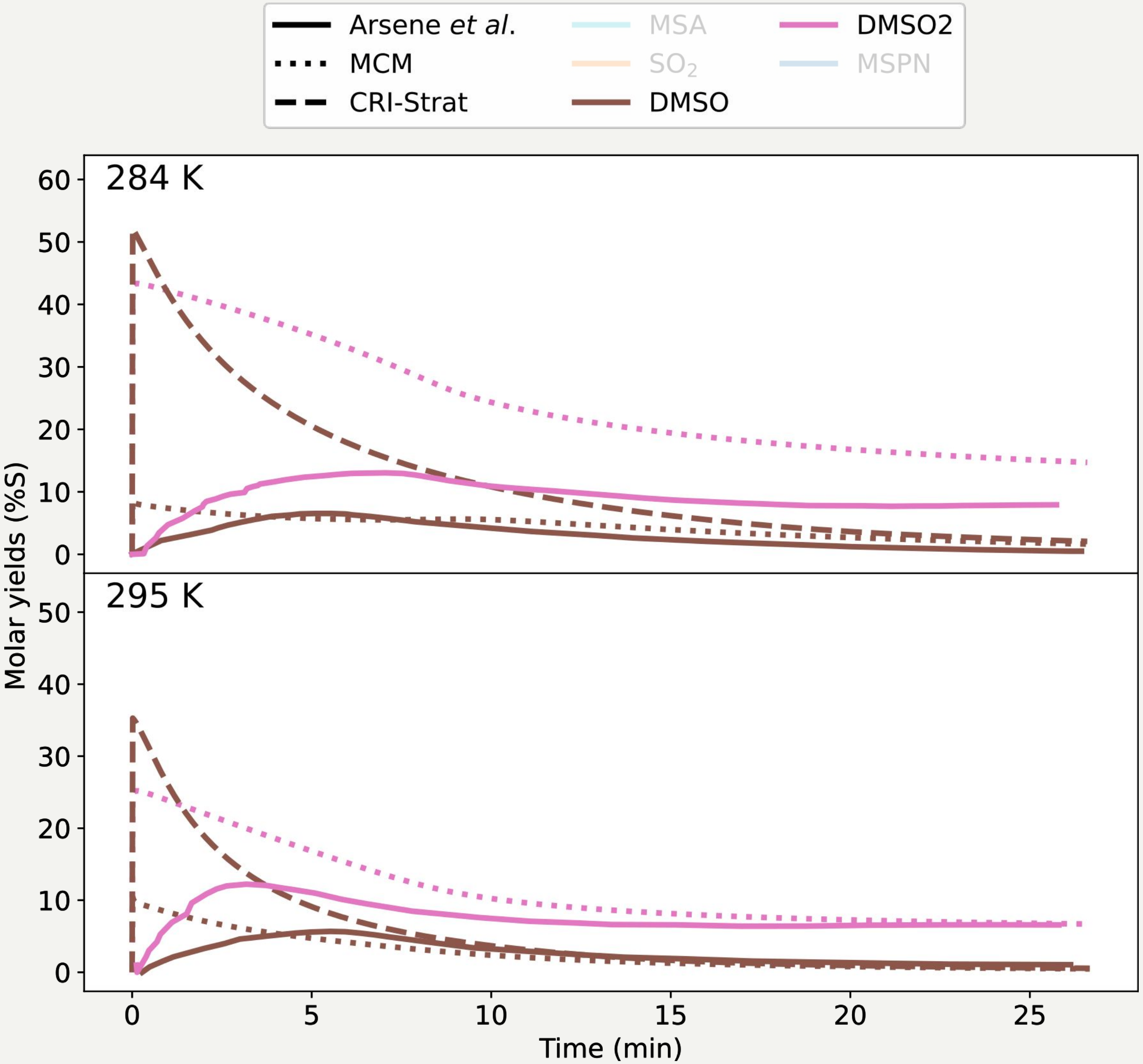
Master Chemical Mechanism (MCM):
- 17,000 reactions
- 81 sulfur-based reactions
- Good for simple models: box models

Common Representative Intermediates (CRI):
- 1183 reactions
- 38 sulfur-based reactions
- Good for more complicated models: global atmospheric models



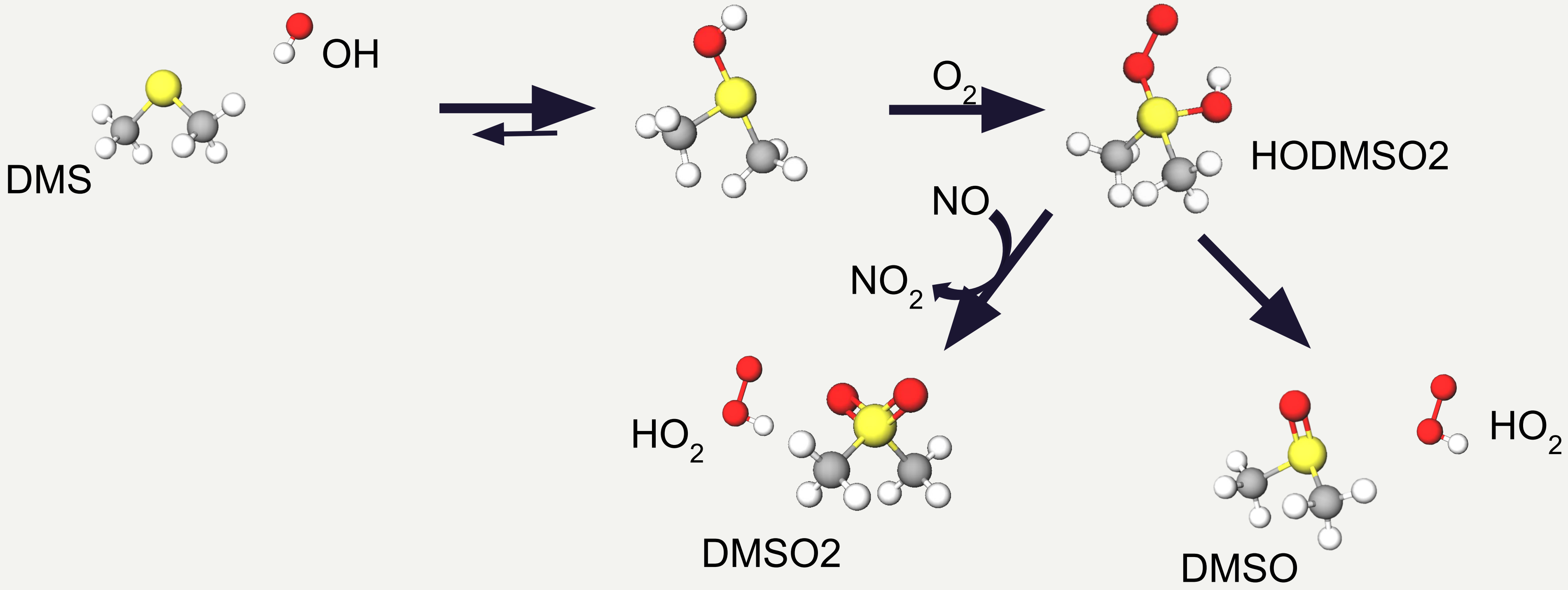
Comparing the mechanisms to experiments: Arsene *et al.*

Experimental Conditions:
DMS conc.: 6.5 ppm
H_2O_2 conc.: 25 ppm
NO_2 conc.: 350-500 ppb
NO conc.: 900-1100 ppb
Bath gas: synth. air
Total pressure: 1000 mbar



Arsene, C.; Barnes, I.; Becker, K. H.; Mocanu, R. *Atmos. Environ.* **2001**, 35, 3769-3780.

The MCM includes an additional reaction, forming DMSO2



CRI-Strat:

DMS + OH = DMSO + HO_2 $\quad 9.5\times10^{-39}[O_2]e^{5270/T}/(1+7.5\times10^{-29}[O_2]e^{5610/T})$

CRI-Strat Updated

DMS + OH = $HODMSO_2$ $\quad 9.5\times10^{-39}[O_2]e^{5270/T}/(1+7.5\times10^{-29}[O_2]e^{5610/T})$

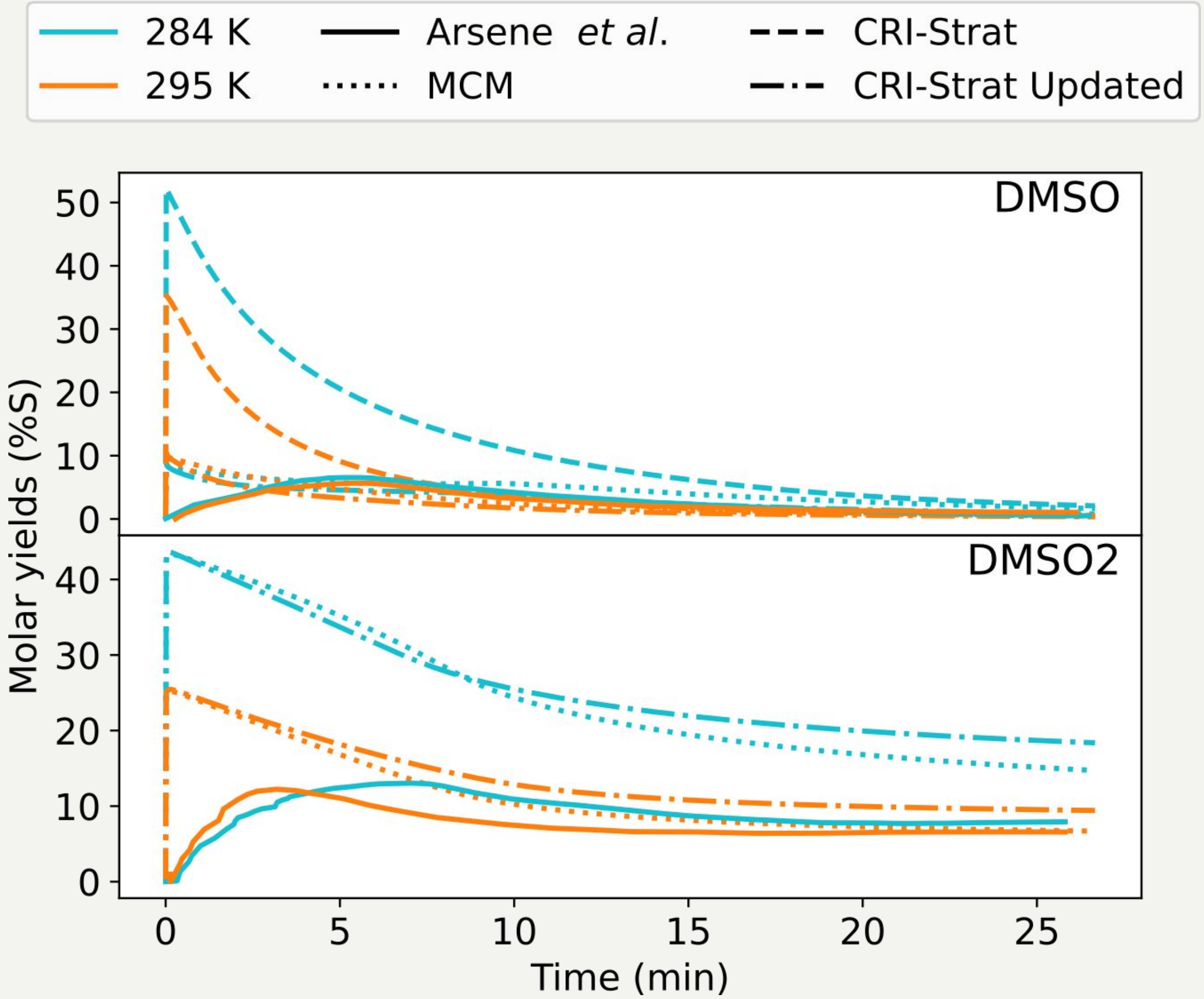
$HODMSO_2$ = DMSO + HO_2 $\quad 8.90\times10^{10}e^{-6040/T}$

$HODMSO_2$ + NO = DMSO2 + HO_2 + NO_2 $\quad 2.7\times10^{-12}e^{360/T}$

Adding a few reactions made a big difference to the output

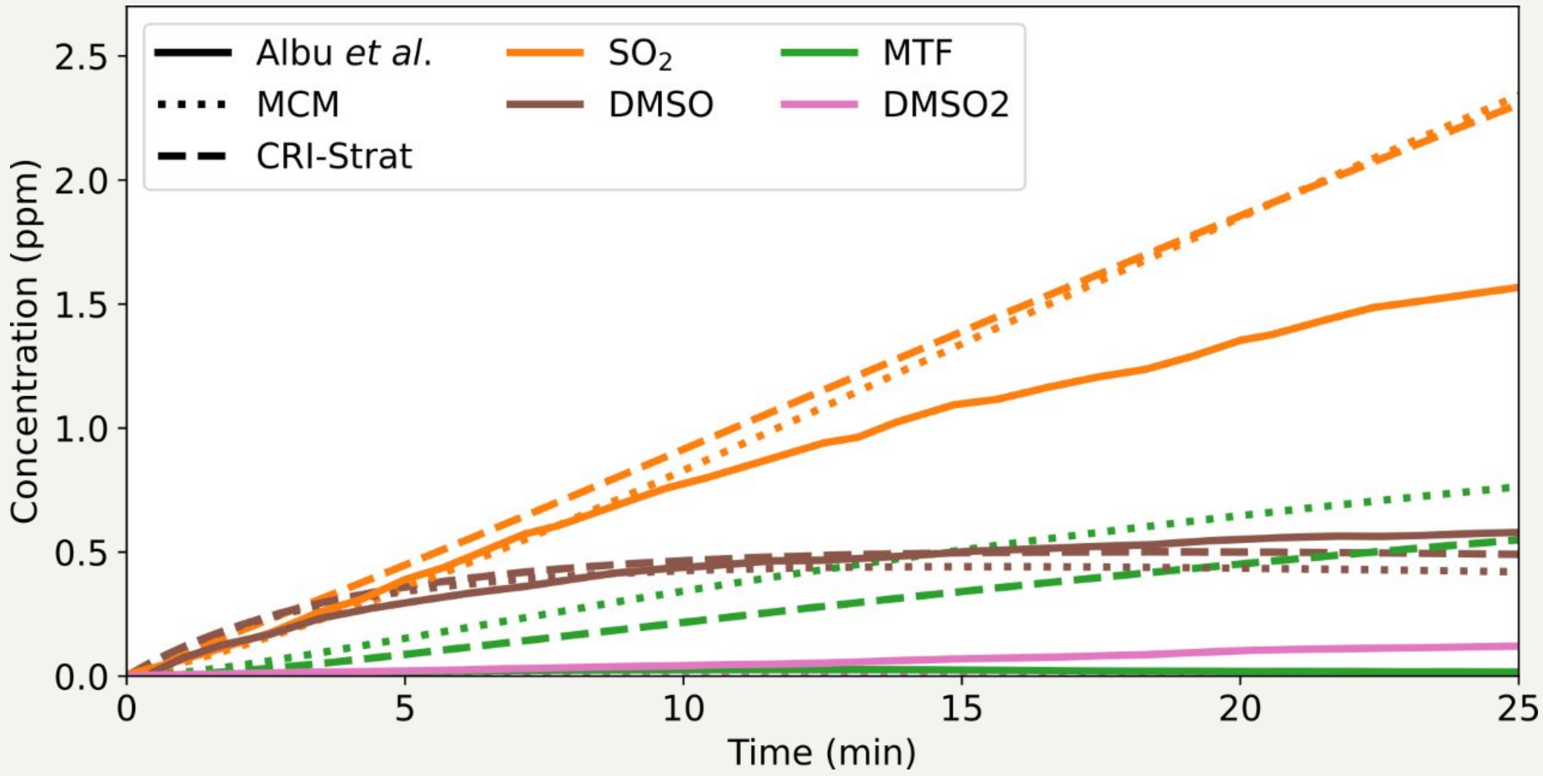
CRI-Strat:
DMS + OH = DMSO + HO_2

CRI-Strat Updated:
DMS + OH = $HODMSO_2$
$HODMSO_2$ = DMSO + HO_2
$HODMSO_2$ + NO = $DMSO_2$ + HO_2 + NO_2



Arsene, C.; Barnes, I.; Becker, K. H.; Mocanu, R. *Atmos. Environ.* **2001**, 35, 3769-3780.

Albu et al: NO free experiment, still sees DMSO2

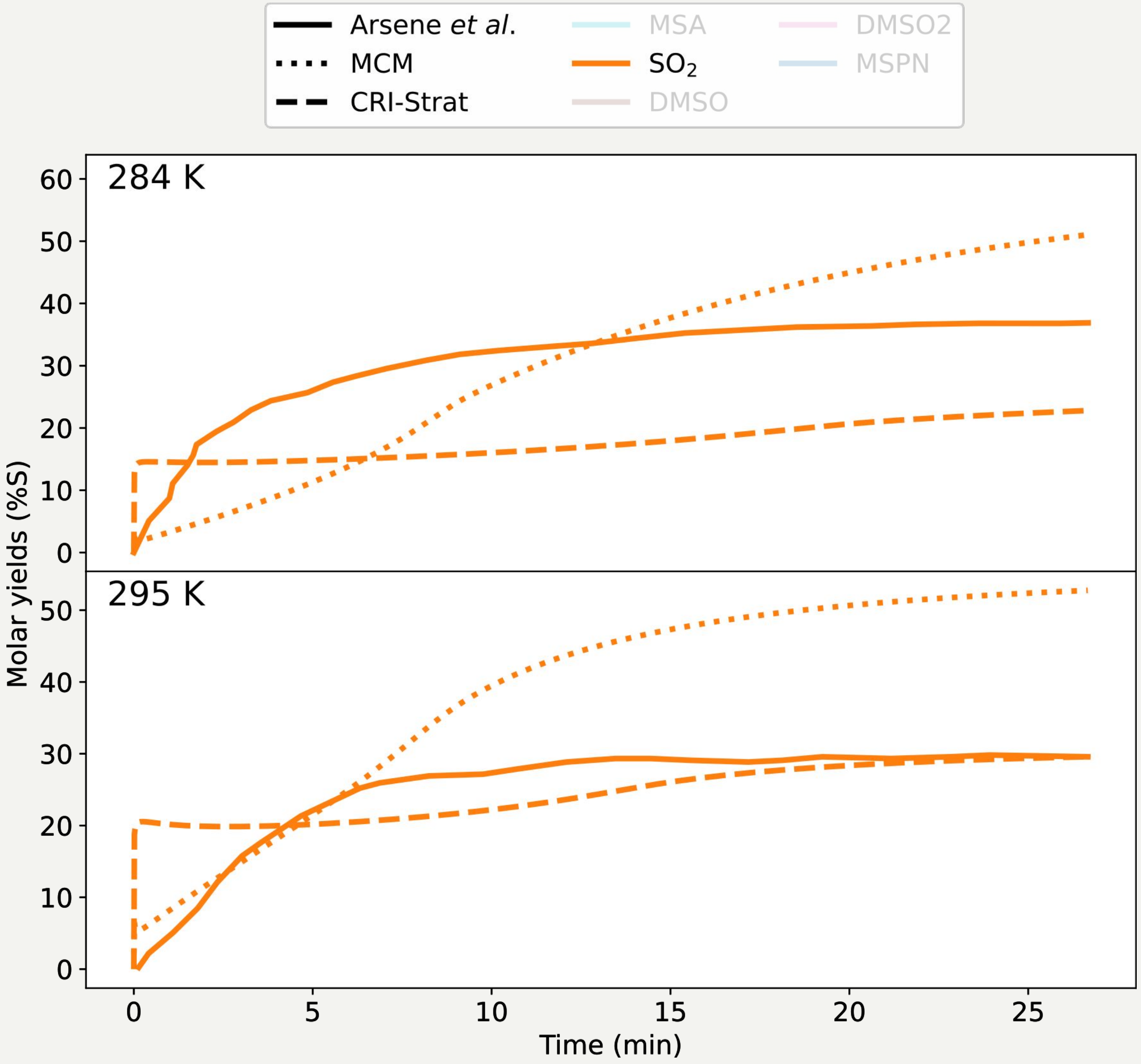


Experimental Conditions:
Temp: 290 K
DMS conc.: 15 ppm
H_2O_2 conc.: 25 ppm
Bath gas: synth. air
Total pressure: 1000 mbar

RO_2 reaction?

Albu, M.; Barnes, I.; Becker, K. H.; Patroescu-Klotz, I.; Benter, T.; Mocanu, R. *In Simulation and Assessment of Chemical Processes in a Multiphase Environment,* Barnes, I., Kharytonov, M. M., Eds.; Springer Science: Dortdrecht, 2008, pp 501-513.

Comparing the mechanisms to experiments: Arsene *et al.*



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H_2O_2 conc.: 25 ppm
NO_2 conc.: 350-500 ppb
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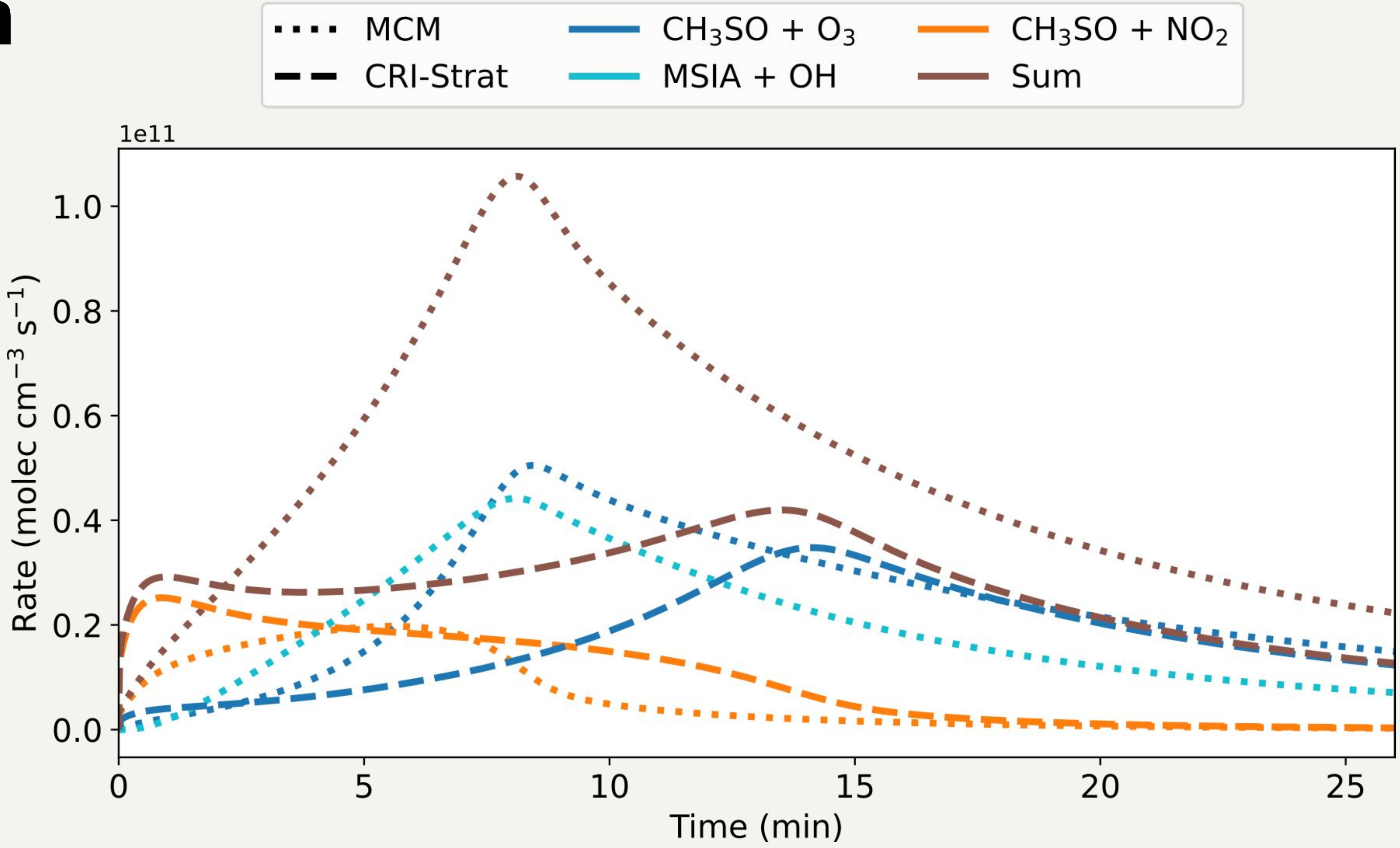
Bath gas: synth. air
Total pressure: 1000 mbar

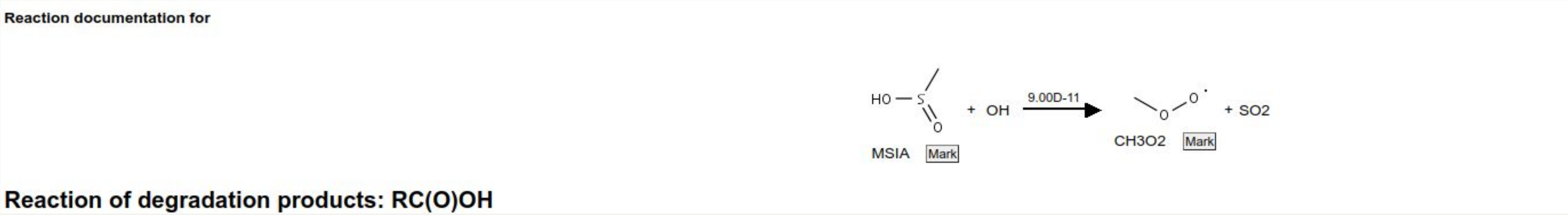
Arsene, C.; Barnes, I.; Becker, K. H.; Mocanu, R. *Atmos. Environ.* **2001**, 35, 3769-3780.

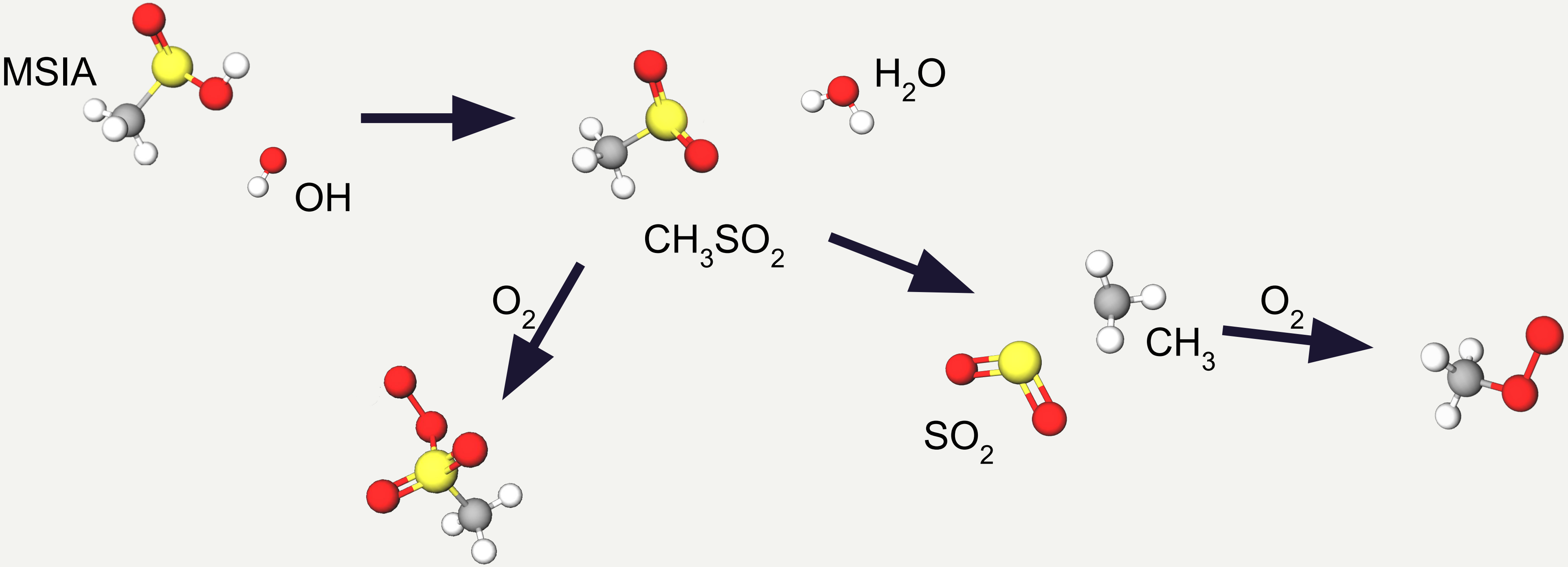
The differences in SO_2 formation can be explained by the reactions



Arsene, C.; Barnes, I.; Becker, K. H.; Mocanu, R. *Atmos. Environ.* **2001**, 35, 3769-3780.

The MCM assumes sulfur chemistry is similar to RC(O)OH

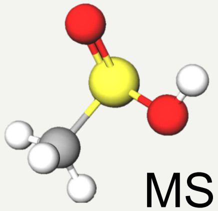


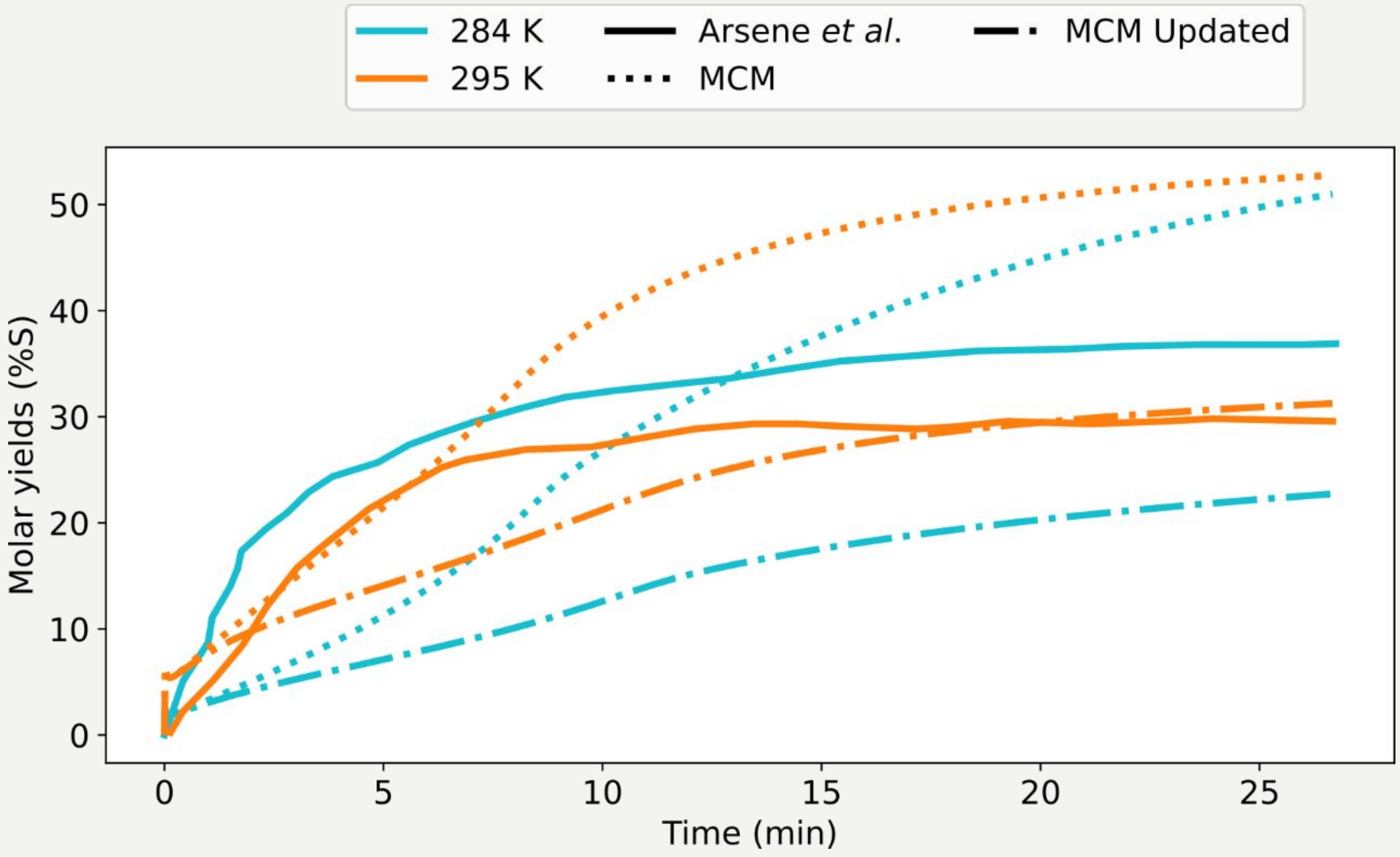


In the case of SO2, one reaction is key:

MCM:
MSIA + OH = $CH_3O_2 + SO_2$

MCM Updated:
MSIA + OH = CH_3SO_2





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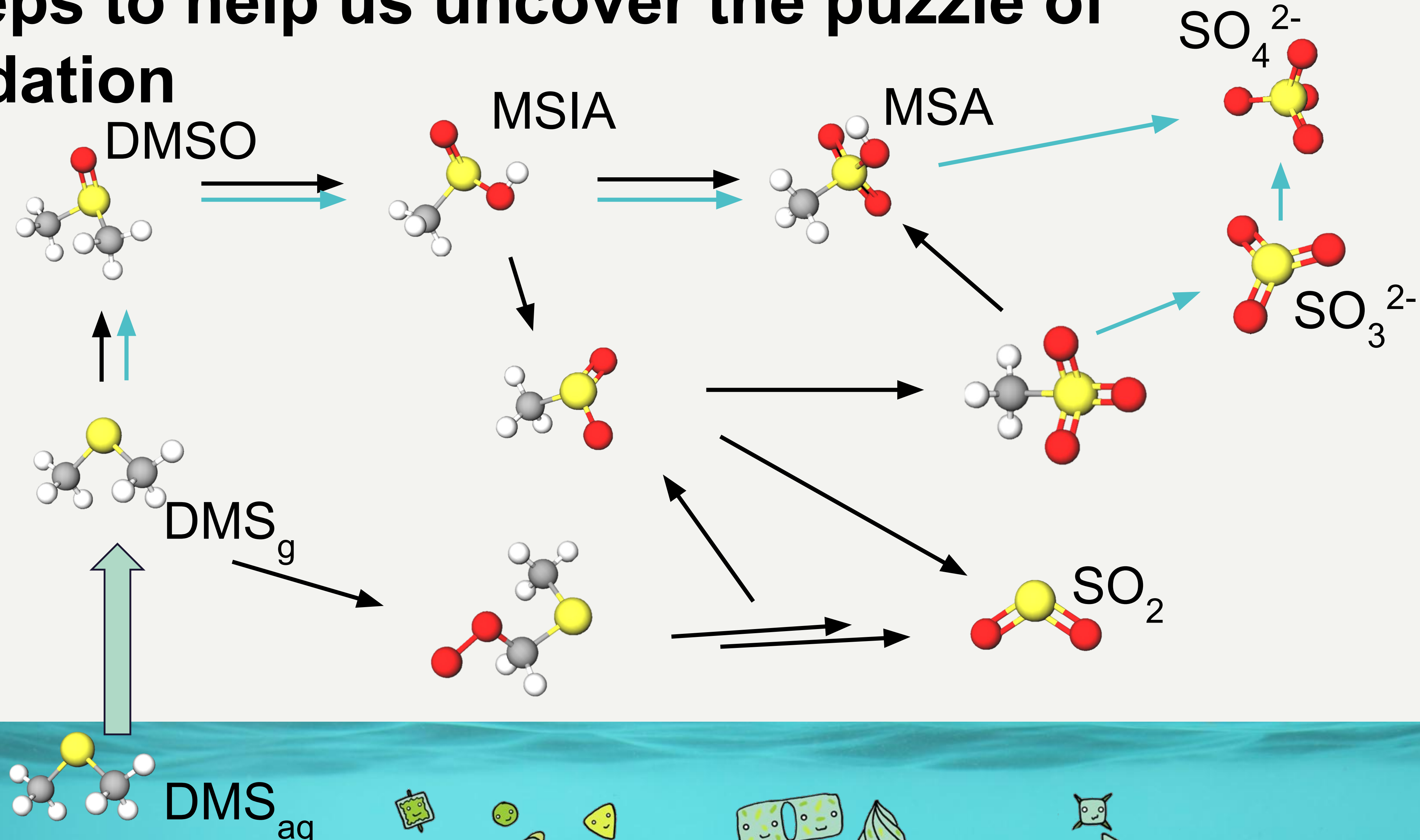
Small steps to help us uncover the puzzle of DMS oxidation



Acknowledgements

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Dr. Chiara Giorio

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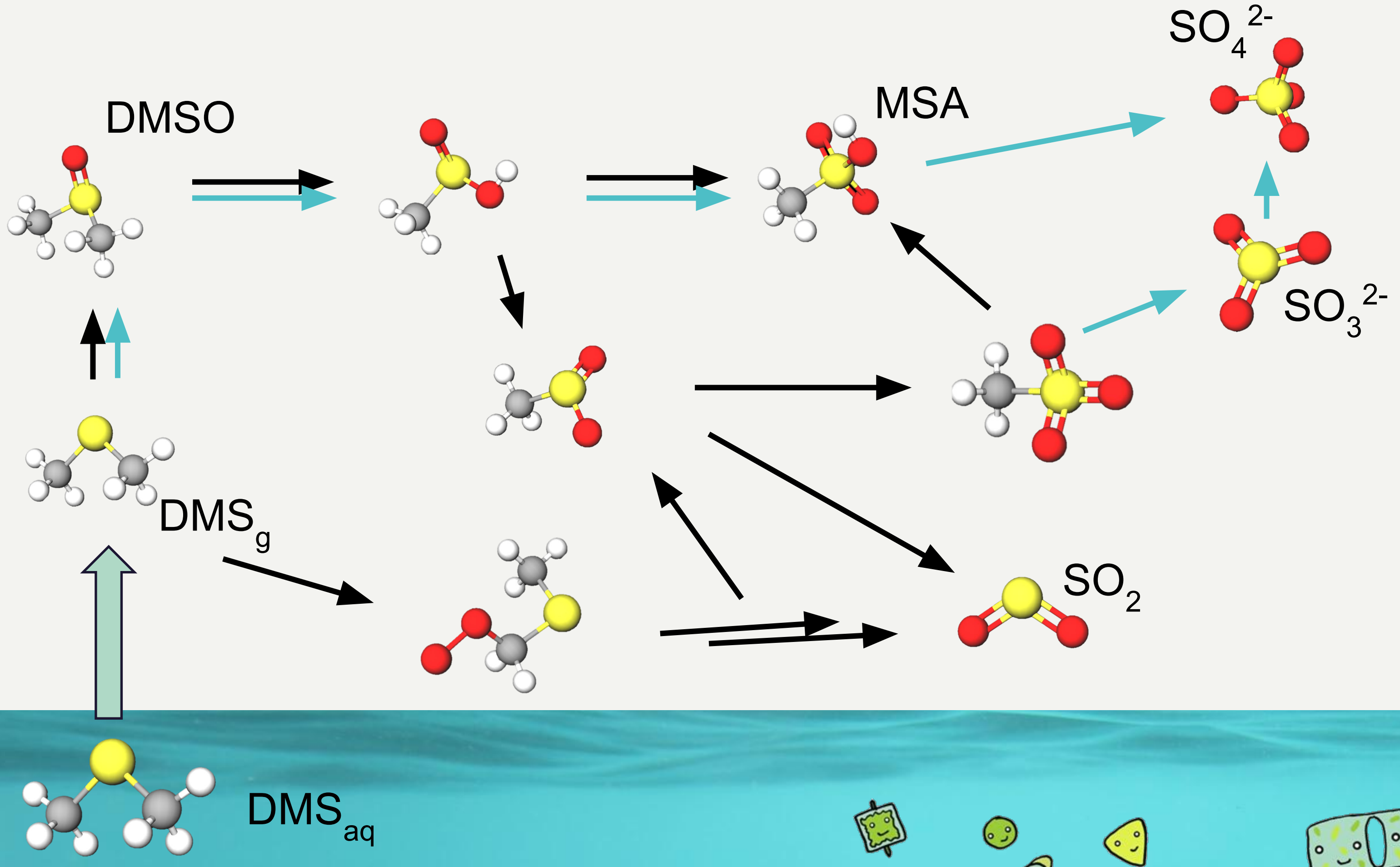
Talk about the state of what's in the models
- currently they are all over the place
- can we constrain the models by going back to older experiments
- compare Ben's study, showing a more qualitative evaluation (which is what is generally done on a global scale), to this, which is more of a quantitative assessment

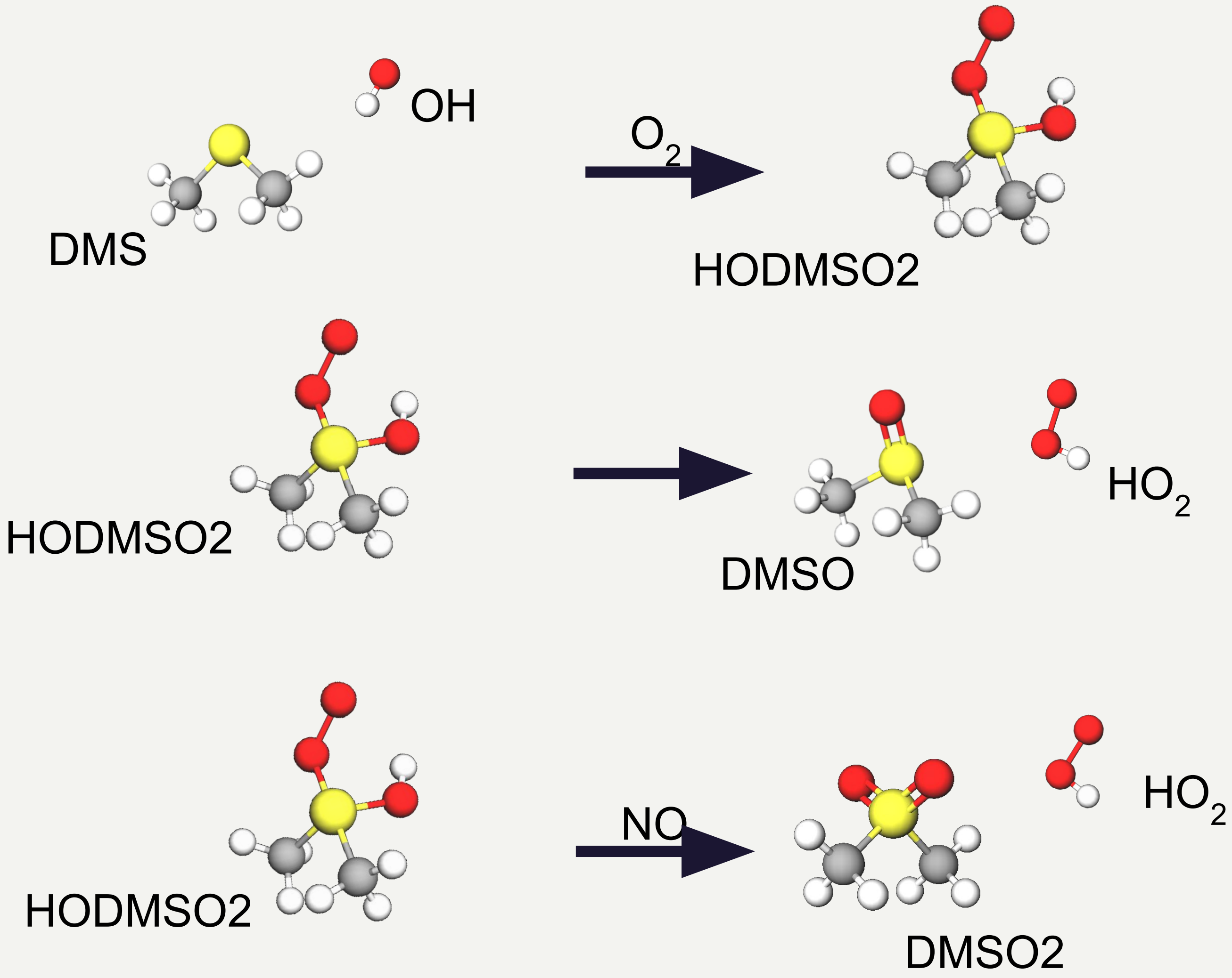
The modelling of DMS oxidation is only as good as our knowledge of the chemistry



Aim: To improve the modelling of DMS oxidation chemistry

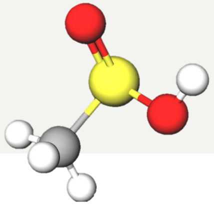
Objectives:

1. Assess the current uncertainties in the DMS oxidation pathway using box modelling
2. Perform fieldwork that can be compared to the atmospheric models
3. Assess the use of MSA as an ice core proxy using global atmospheric models

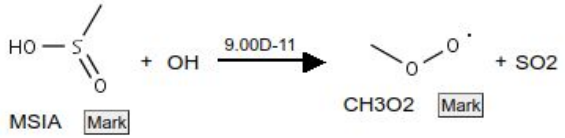


CRI-Strat:
DMS + OH = DMSO + HO2

CRI-Strat Updated:
DMS + OH = HODMSO2
HODMSO2 = DMSO + HO2
HODMSO2 + NO = DMSO2 + HO2 + NO2



Reaction documentation for

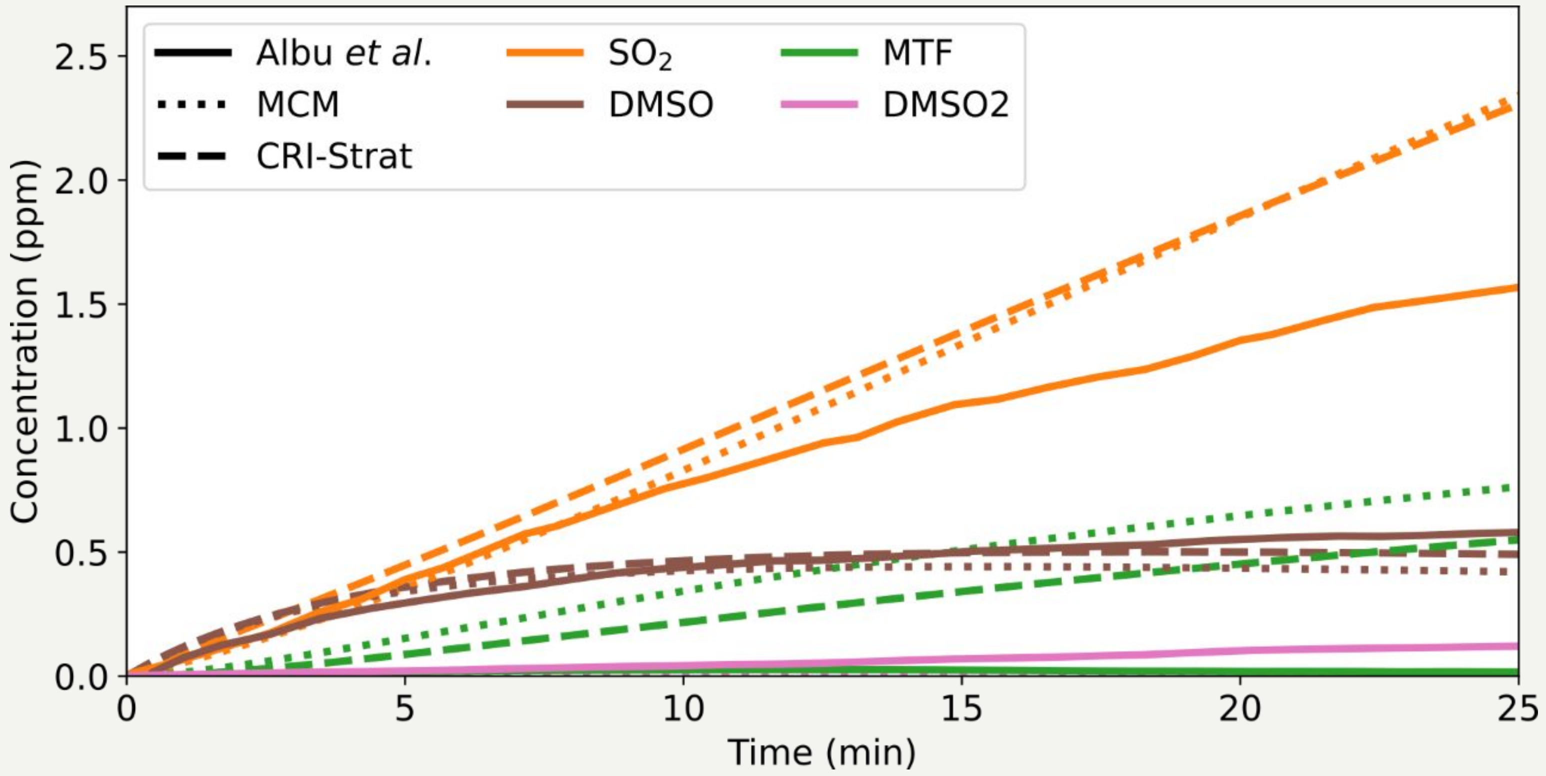


Reaction of degradation products: RC(O)OH

One study that this relies on had 100% formation of SO_2, however, that was done in the oxygen free experiment. In a bath gas of neat N_2, the formation of CH_3SO_2 solely forms the above (CH_3 + SO_2) though with oxygen (or O_3 and NO_2) other products could be found

								MCM	CRI Strat
8	CH3SO2	+	O3	=	CH3SO3			3.00D-13	3.0D-13
9	CH3SO2			=	CH3O2	+	SO2	5.00D+13*EXP(-9673/TEMP)	5.00D13*EXP(-9673/TEMP)
10	CH3SO2	+	O2	=	CH3SO2O2			1.03D-16*EXP(1580/TEMP)*O2	
11	CH3SO2	+	NO2	=	CH3SO3	+	NO		2.2D-12

Comparing the mechanisms to experiments: Albu et al.



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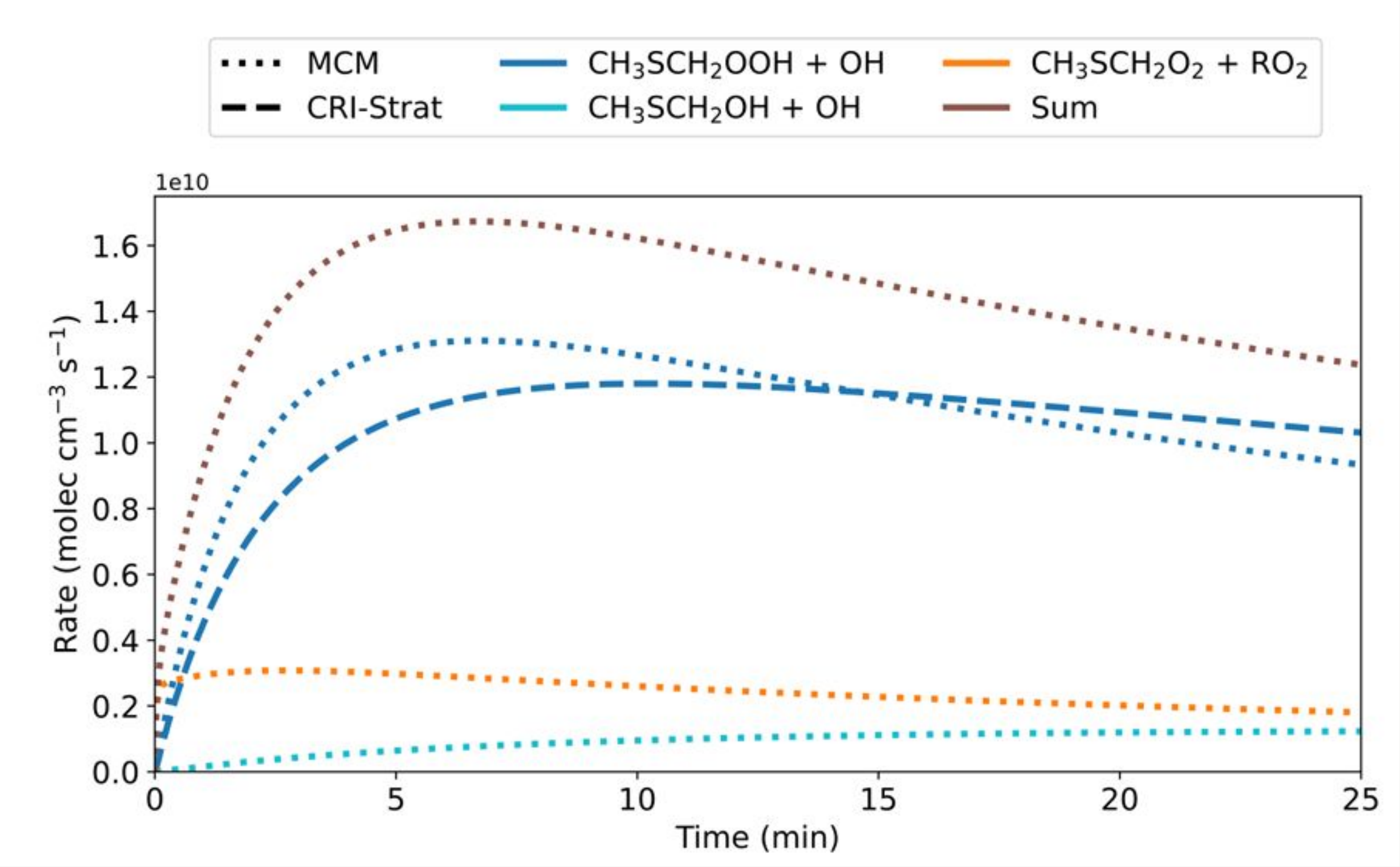
Looking into the differences of MTF



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