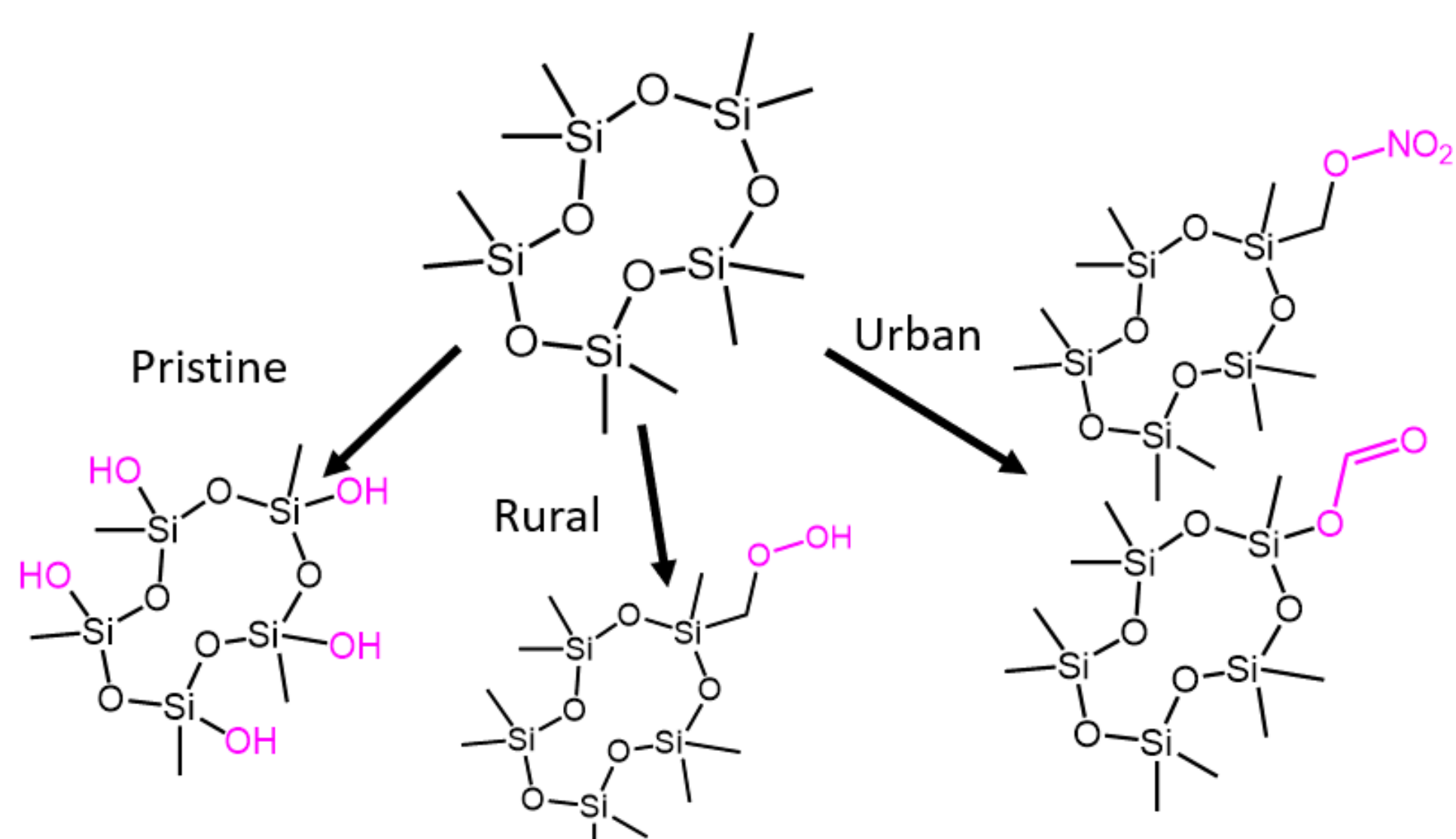


Investigation of the Volatile Methyl Siloxane Oxidation Mechanism in Urban and Remote Atmospheric Conditions

Mitchell Alton*, Eleanor Browne

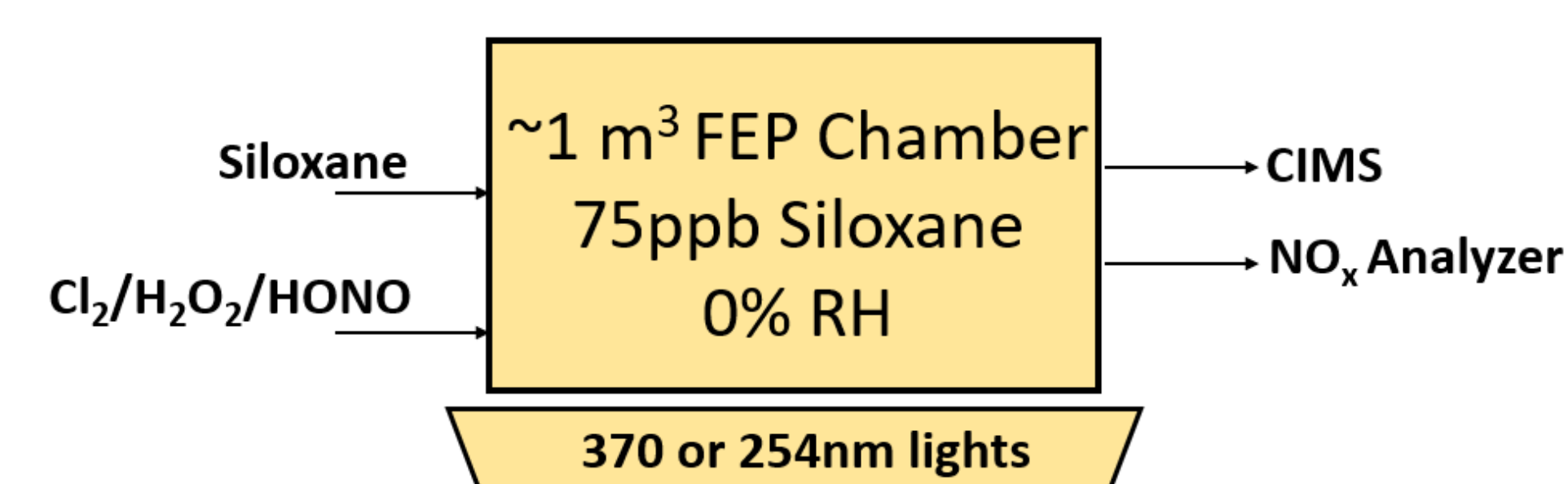
Introduction

- More than two million tons of volatile methyl siloxanes (VMS) are produced globally each year¹
- Due to their high vapor pressures and low water solubilities, >90% of released VMS partition into the atmosphere - gas phase oxidation dominates the environmental loss of these compounds²
- VMS are oxidized by hydroxyl (OH) radicals and chlorine (Cl) atoms, quickly forming a compound called a peroxy radical, with different products formed from this radical³
- Little is known about the fate of this peroxy radical and how it forms previously observed oxidation products, limiting our understanding of the environmental fate of these compounds

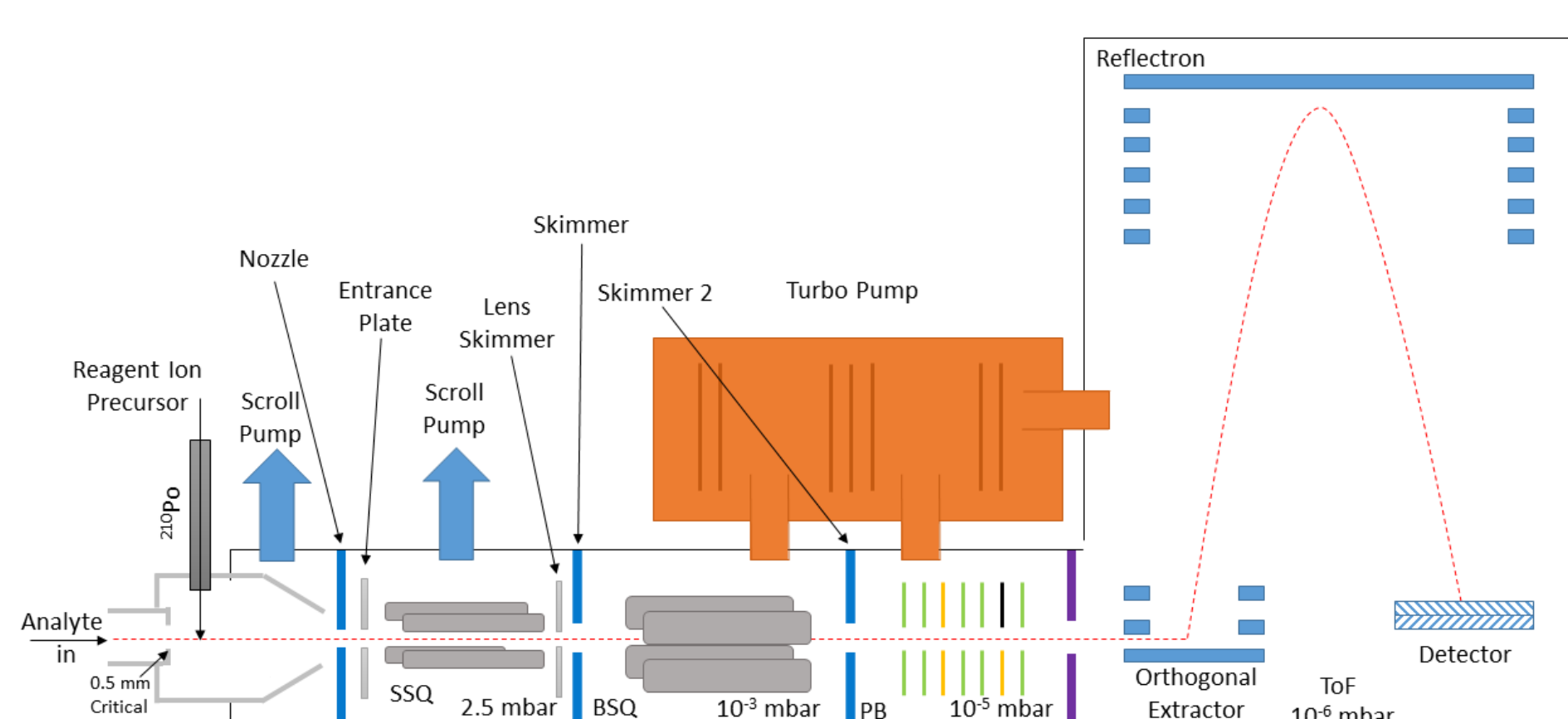


Methods

- 3 cyclic VMS were oxidized by photolyzing either Cl₂, H₂O₂, or HONO



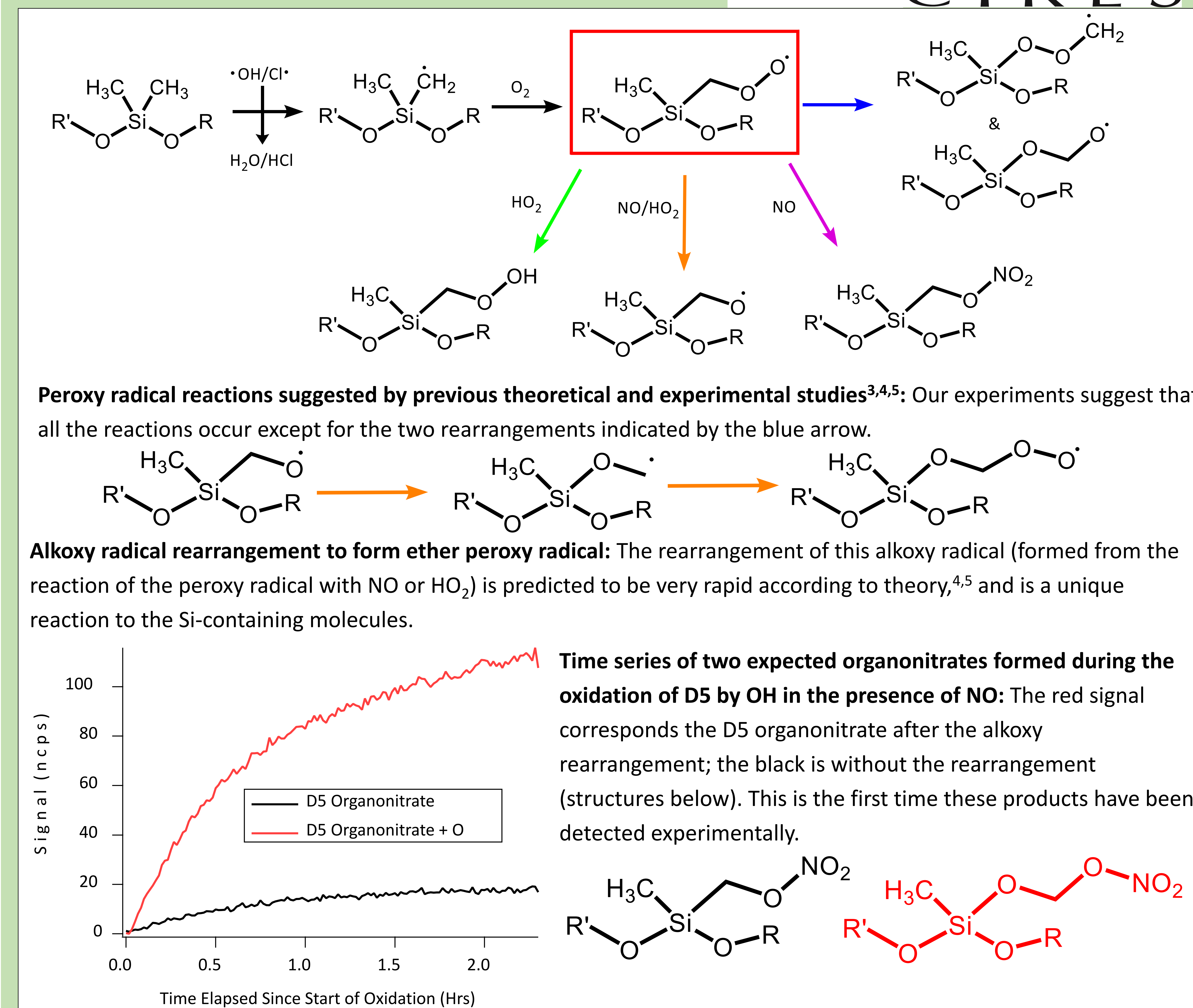
- Chamber (diagram above) was partially collapsed during the experiment, reducing the total volume by ~10%



- Diagram of CIMS' ionization region and ion optics

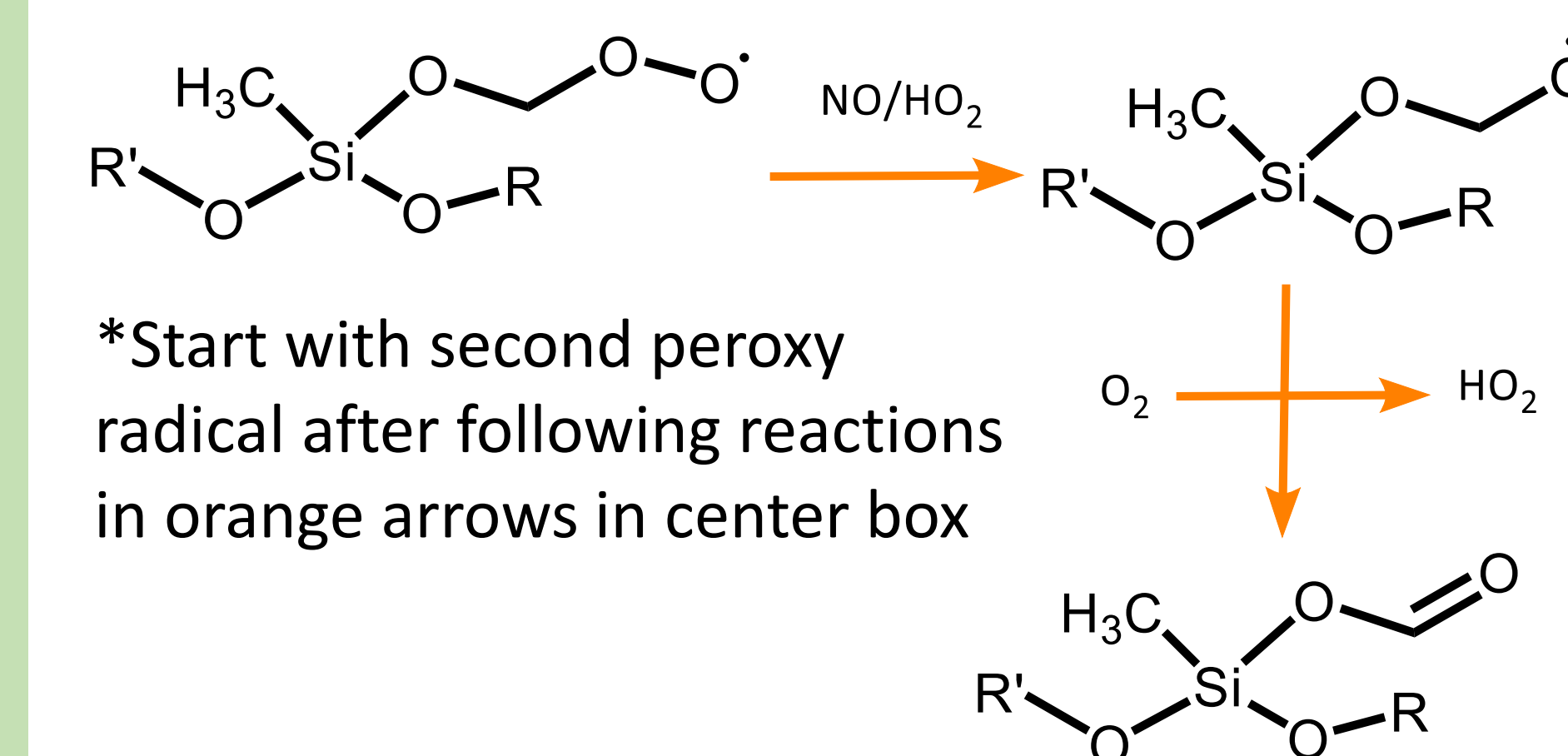
Characterization of VMS oxidation reveals unexpected oxidation mechanism. Additional oxygen incorporation could affect aerosol partitioning and environmental impacts

Have more questions? Want to talk more? [Click here to leave contact info!](#) Or follow additional URL.



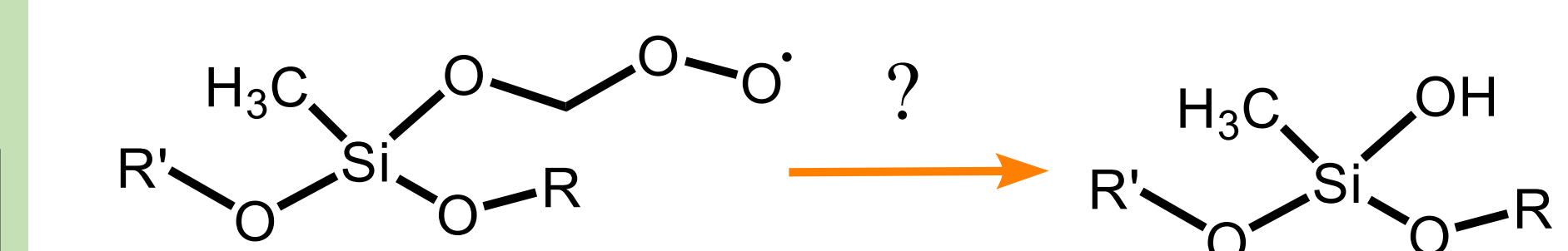
Formation of silyl ester and silanol:

- Two main products previously detected: silanol and silyl esters
- Unclear how to form the silanol from peroxy radical



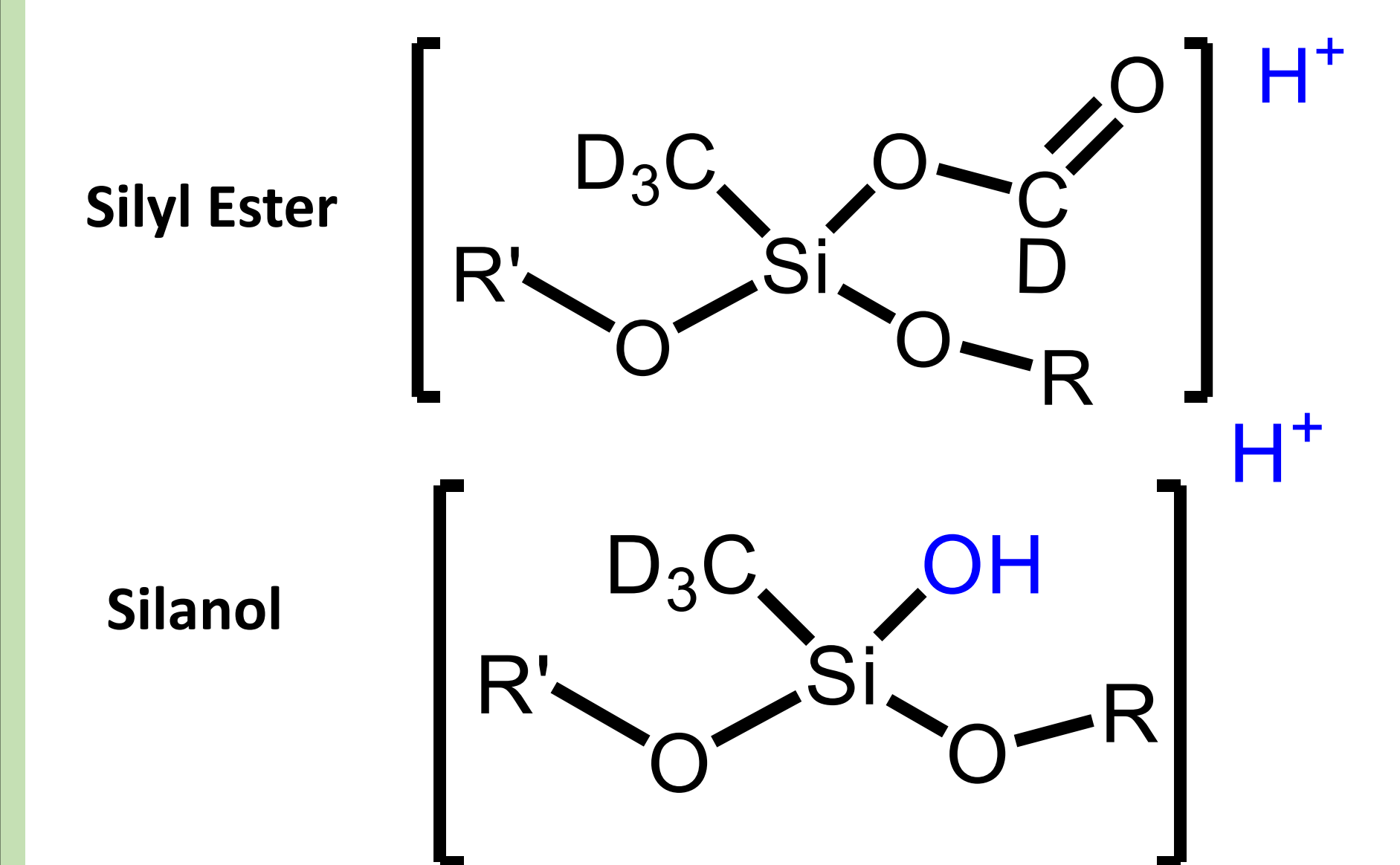
*Start with second peroxy radical after following reactions in orange arrows in center box

- Silanol is formed in higher levels with shorter RO₂ lifetimes
- Suggests a branching ratio at the second peroxy radical, as the first peroxy radical is likely to lose the terminal oxygen atom
- Mechanism for this transformation is still unclear



Deuterated L2 (D₁₈L2) Oxidation as silyl ester structure confirmation

- Isotopically labeled VMS can assist with structure identification from molecular formulas
- Oxidized D₁₈L2 with Cl atoms
- Charge carrier is always a proton from toluene
- Any other protons in the molecular formula are from H exchanges with ambient water
- Aldehydic H/D do not exchange with water, alcoholic H/D do
- Main product structures shown below, with only one or two protons, validating the structures



*Mitchell.Alton@Colorado.edu
Department of Chemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, UCB 215, Boulder, CO 80309

- [1] D. Brooke et al., *Environmental Risk Assessment Report: Decamethylcyclopentasiloxane*, 2009.
- [2] C. Rücker, K. Kümmerer, *Environmental Chemistry of Organosiloxanes*, 2015.
- [3] R. Atkinson et al., *Kinetics and products of the gas-phase reactions of (CH₃)₄Si, (CH₃)₃SiCH₂OH, (CH₃)₃SiOSi(CH₃)₃ and (CD₃)₃SiOSi(CD₃)₃ with Cl atoms and OH radicals*, 1995
- [4] Z. Ren, G. da Silva, *Auto-Oxidation of a Volatile Silicon Compound: A Theoretical Study of the Atmospheric Chemistry of Tetramethylsilane*, 2020
- [5] Z. Fu et al., *Formation of Low-Volatile Products and Unexpected High Formaldehyde Yield from the Atmospheric Oxidation of Methylsiloxanes*, 2020