Night-time aircraft measurements of OH and HO_2 using the FAGE technique

Hannah Bunyan*, Trevor Ingham, Daniel Stone, Stewart Vaughan, Mathew Evans and Dwayne Heard
*(cmhmb@leeds.ac.uk), *School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK*
UNIVERSITY OF LEEDS

1 Introduction

Night-time oxidation chemistry

- The hydroxyl radical, OH, dominates day-time oxidation of trace gases in the troposphere. Night-time oxidation is thought to be driven by the nitrate radical, NO_3 (Geyer *et al.*, 2003)
- OH and HO_2 are produced at night *via* ozone- and NO_3-initiated alkene oxidation

The RONOCO Project

- **RONOCO**: Role of night-time chemistry in controlling the oxidising capacity of the atmosphere
- Aims: to advance our understanding of night-time chemistry and impact on the troposphere
- Measurements of gas- and aerosol-phase composition made onboard BAe-146 research aircraft
- Two measurement campaigns conducted from East Midlands Airport, UK, July 2010 and January 2011

Aims and questions

- Measure concentrations of OH and HO_2 at night
- What are the dominant HO_x – producing species at night?
- Is NO_3 a propagator/chain carrier of night-time OH and peroxy radical production?
- How do aerosol and NO_3 impact HO_x?

2 The Leeds FAGE Aircraft Instrument

- **FAGE**: Fluorescence Assay by Gas Expansion (Commane *et al.*, 2010)
- Laser-induced fluorescence at low pressure (~ 1.8 Torr)
- Specialised inlet mounted in a window blank; ambient air sampled from outside the aircraft through 0.7 mm pinhole
- OH excited from ground state, $X^2\Pi$, to first electronically excited state, $A^2\Sigma$, using light at $\lambda \sim 308$ nm
- On-resonance fluorescence detected by temporal gated photon counting
- HO_2 detection by chemical conversion to OH using an excess of NO:

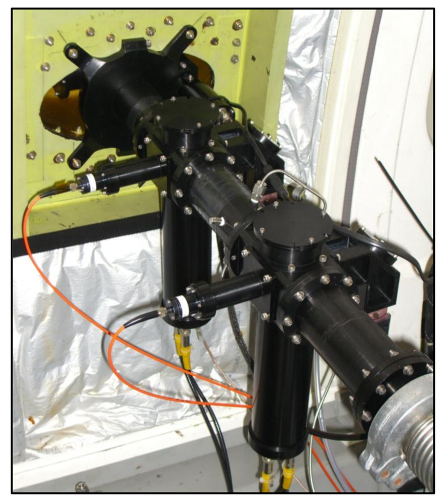
$$HO_2 + NO \rightarrow OH + NO_2$$

- Calibration with a known concentration of OH and HO_2:

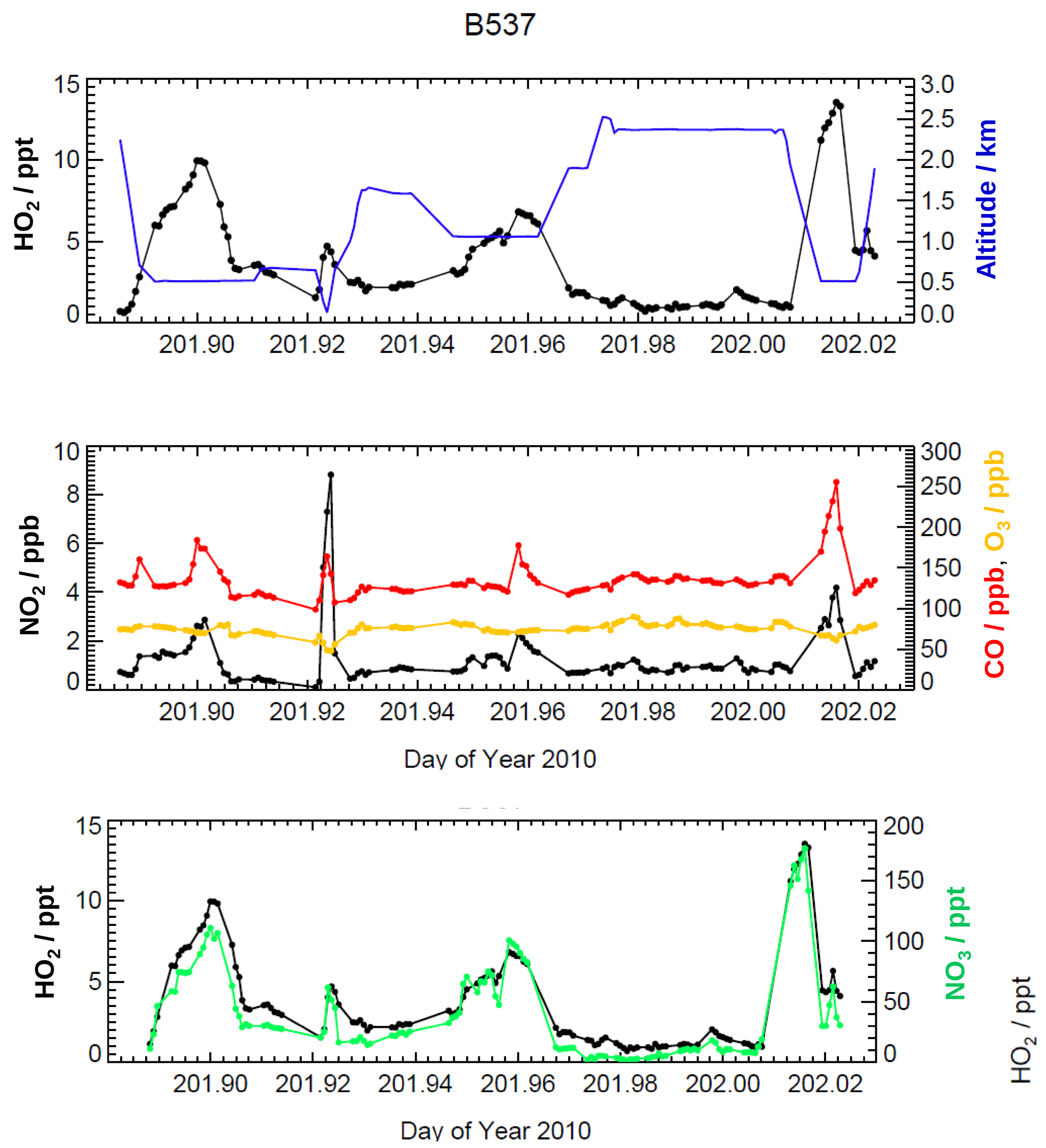
$$H_2O + hv\ (\lambda = 185\ \text{nm}) \rightarrow OH + H$$

$$H + O_2 \xrightarrow{M} HO_2$$

BAe-146 Research Aircraft, with HO_x inlet circled in red

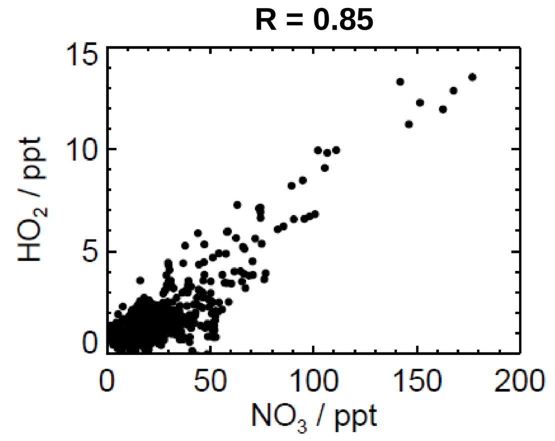

FAGE detection assembly installed on BAe-146 aircraft

3 Measurements

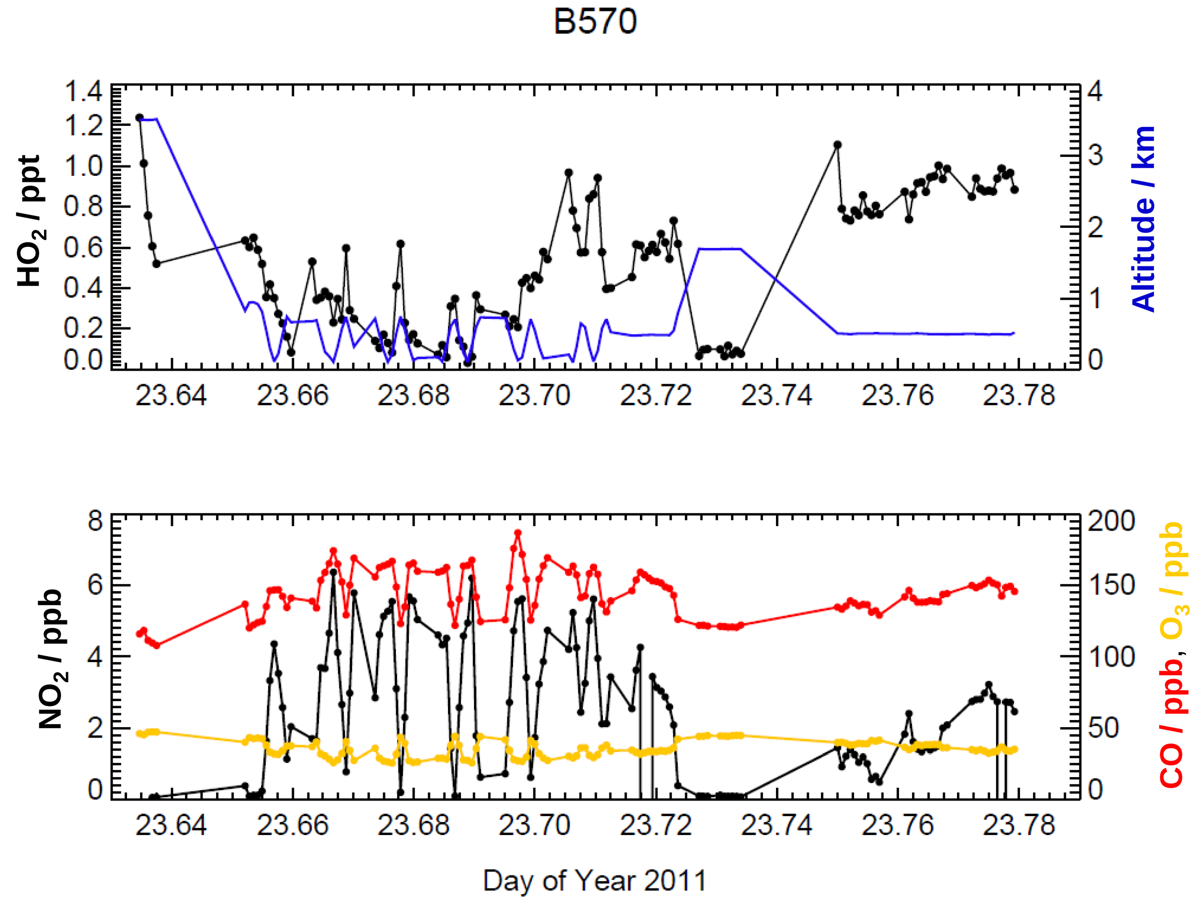


Night-time flight, 20th July 2010. Low-level flying off Norfolk Coast and Thames Estuary. High $[O_3]$, [CO] and $[HO_2]$. Excellent correlation (R = 0.97) between HO_2 and NO_3. $[HO_2]$ shows positive correlation with $[NO_2]$ and [CO] and negative correlation with $[O_3]$.

- Highest night-time $[HO_2]$ ~ 13 ppt, measured during flight B537 (see figure, left)
- OH was not detected at night above the instrument's limit of detection during the summer and winter campaigns
- RO_2 radicals from alkenes are a potential source of interference in FAGE measurements of HO_2 (Fuchs *et al.*, 2011)



Summer flights show good correlation with NO_3



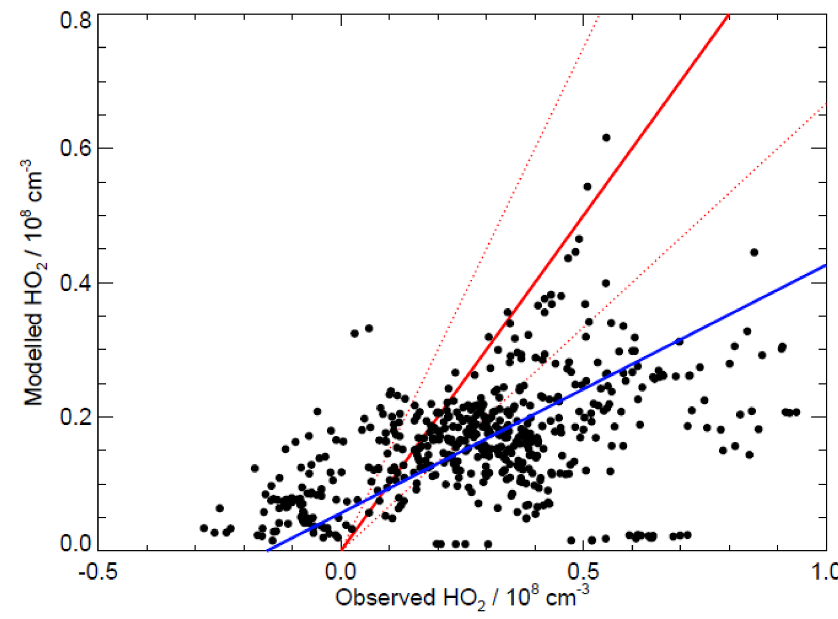
Dusk into night-time flight, 23rd January 2011. Low level vertical saw-tooth pattern along South Coast. Small modulations in $[HO_2]$ with altitude. $[HO_2]$ shows negative correlation with $[NO_2]$ and [CO] and positive correlation with $[O_3]$.

		Average Mixing Ratio / ppt	Average Concentration / molecule cm^{-3}	Limit of Detection / molecule cm^{-3}
Summer	OH	0.04	8.9×10^5	1.8×10^6
	HO_2	1.6	3.7×10^7	6.9×10^5
Winter	OH	0.005	1.2×10^5	6.4×10^5
	HO_2	0.7	1.7×10^7	6.0×10^5

Summary of measurements

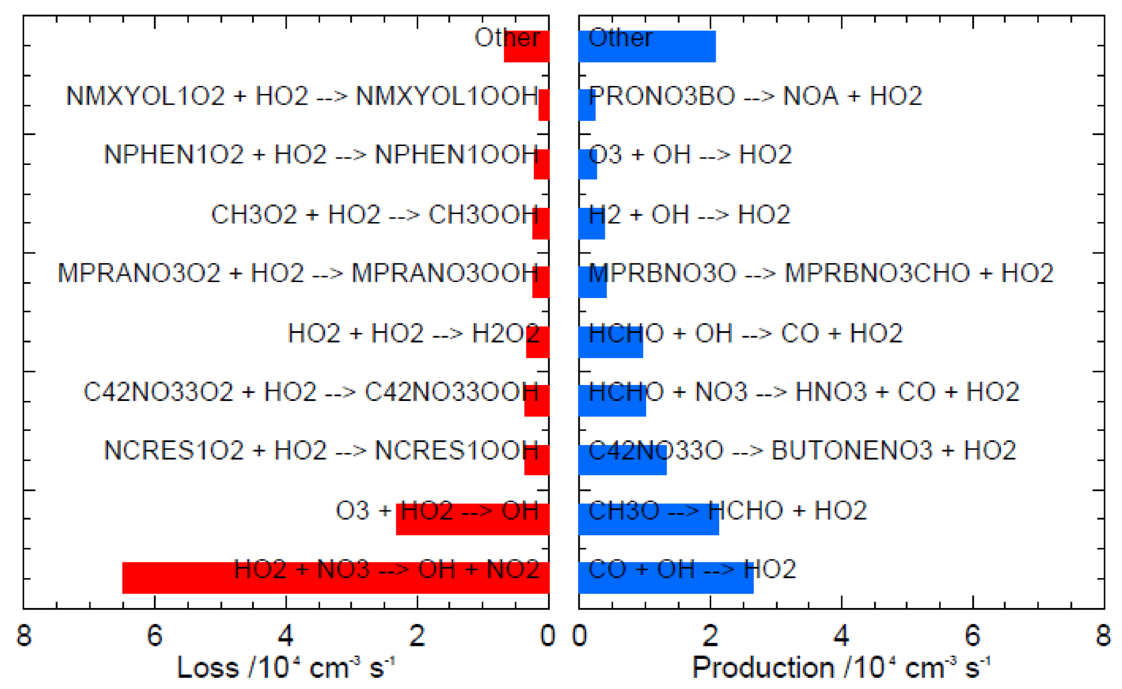
4 Modelling

- **DSMACC** Box Model: Dynamically Simple Model of Atmospheric Chemical Complexity (Emmerson and Evans, 2009, Stone *et al.*, 2010)
- Observationally constrained box model run to steady state
- Chemistry scheme from Master Chemical Mechanism (MCM) (Jenkin *et al.*, 2003, Saunders *et al.*, 2003)
- What is controlling HO_x at night?
- Can we explain observations of OH and HO_2 at night?
- What processes are controlling production and loss of HO_x?
- Mean modelled OH = 6×10^4 molecule cm^{-3} (summer flights only), consistent with observations

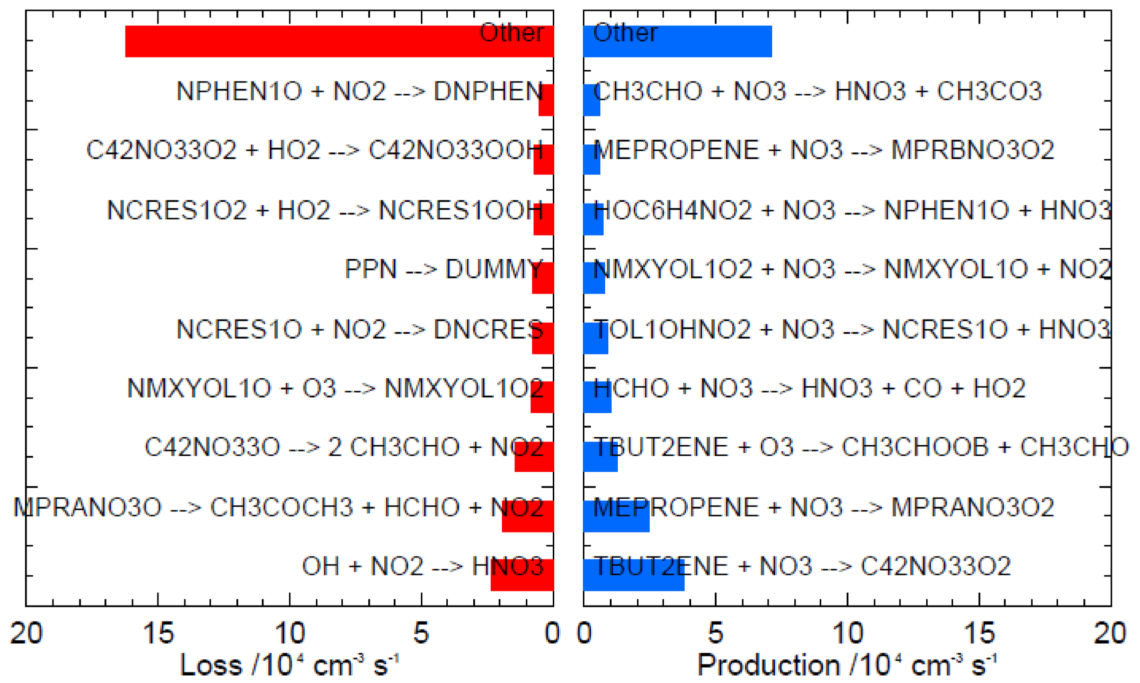


Comparison between observed and modelled HO_2.
1:1 Line (± 50%), Line of Best Fit:
$[HO_2]_{mod} = \{(0.36 \pm 0.03)\ [HO_2]_{obs}\} + (0.06 \pm 0.01)$
$r^2 = 0.22$

Rate of Production and Loss of HO_2

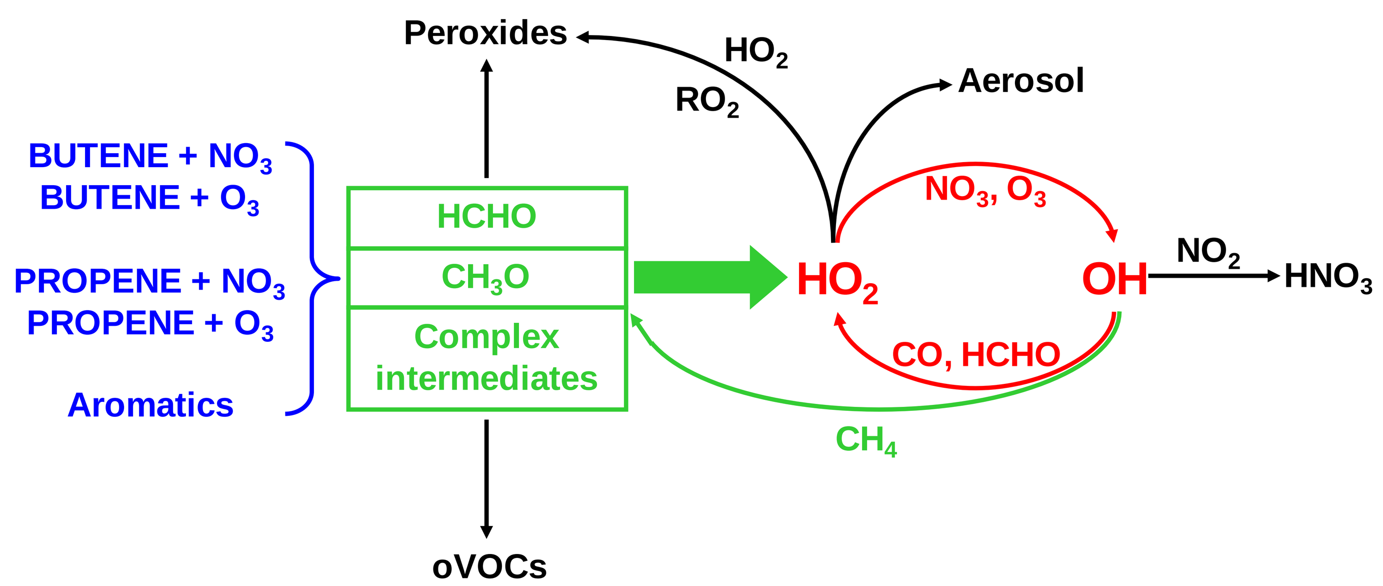


Processes controlling HO_2 in the model.
HO_2 production from CO + OH, $CH_3O + O_2$, HCHO + OH/NO_3
Loss by $HO_2 + NO_3$, O_3 + OH, HO_2 + RO_2
Many of these reactions are not net sources or sinks of radicals.



Processes controlling RO_x (radical sources and sinks) in the model.
Large number of reactions contributing to radical production and loss.
Production from alkenes + O_3, alkenes + NO_3, RCHO + NO_3
Loss by OH + NO_2, decomposition of nitrated radicals, HO_2 + RO_2

5 Conclusions and Outlook



- As predicted by the rate of production and loss analysis, HO_2 correlates well with NO_3
- Night-time radical chemistry is much more complex than day-time
- The model currently underpredicts HO_2
- OH was not detected above the instrument's limit of detection at night
- Laboratory studies are needed to assess potential interference from RO_2
- The model will be used to elucidate the processes controlling HO_x chemistry at night, and to explain the observed concentrations of OH and HO_2

References

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