Factors controlling the oxidative capacity of the troposphere since the Last Glacial Maximum

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GEOS-Chem at and since the Last Glacial Maximum

**GOAL:** Test sensitivity of OH to range of uncertainty in climate and emissions over glacial-interglacial periods

**ICE age Chemistry And Proxies (ICECAP) project**

**Climate**
- GISS ModelE GCM (Schmidt et al., 2006)

**Stratospheric chemistry**
- Linoz (McLinden et al., 2000)

**Tropospheric chemistry**
- GEOS-Chem CTM (v9-01-03) (http://www.geos-chem.org)

**Vegetation**
- BIOME4-TG (Kaplan et al., 2006)

**Fire**
- LMfire (Pfeiffer and Kaplan, 2012)

**Isotope chemistry**
- GEOS-Chem Δ^{17}O offline aerosol CTM (Sofen et al., 2011)

4 climate scenarios
- Present Day (ca. 1990s)
- Preindustrial (ca. 1770s)
- "Warm" LGM (~21ka)
- "Cold" LGM (~21ka)

3 past emission scenarios
- Low Fire
- High Fire
- Fixed Lightning

**Uncertainty in ∆SST @ LGM**

**Fire CO Emissions**
- LMfire [Pfeiffer et al., in prep.]
- Scaled to Charcoal Data [Power et al., 2008]

**Uncertainty in past lightning**

- Lightning NOx

**Lightning Scenario**
- Fixed
- Variable
Net reduced OH burdens in all past atmospheres

OH relatively buffered; our present day consistent with large spread in models

We find **decreased** OH at LGM

Most earlier studies found **increases** necessary to match ice-core methane decreases

What controls OH in our simulations?  Why are we different?  Methane budget implications?
OH sensitive to photolysis, water vapor, emissions

We find a simple linear relationship explains 67% of variability in simulated mean OH across glacial-interglacial periods.

\[
[\text{OH}] \propto J_{O_3} q \frac{S_N}{S_C^{3/2}}
\]

Derived from steady-state equations of the \(O_3\)-CO-HO\(_x\)-NO\(_x\) system following Wang and Jacob [1998], who were able to consider \(J_{O_3}\) and \(q\) as constant.

OH most correlated with \(J_{O_3}\), then \(q\), then \(S_N/(S_C^{3/2})\)
In colder climates:
- Stratospheric circulation decelerates
- Less stratospheric NO\textsubscript{x} & ClO\textsubscript{x}
- Lower tropopause

More tropical overhead ozone (converse in warmer climates)

Earlier studies used present-day stratospheric boundary conditions
Tropospheric H$_2$O changes with surface temperature

Surface and atmospheric temperature decreases drive large decreases in water vapor at LGM relative to preindustrial; small increases in present day.
OH sensitivity to changing emissions

\[ J_{O_3} q \frac{S_N}{S_C^{3/2}} \]

Simulated mean OH 
not sensitive to
- Fires
- Fuel combustion

but sensitive to
- Lightning

Fuel, fire, and biogenics all have correlated changes in \( S_N \) and \( S_C \)

\( R^2 = 1.00 \)
\( R^2 = 0.98 \)
\( R^2 = 0.92 \)
\( R^2 = 0.40 \)

Lightning makes a large percentage of \( S_N \), and \( S_N \ll S_C \); ratio easily perturbed by lightning

Earlier studies did not vary \( S_N \) overhead ozone, favoring \( \Delta S_C \).
**Implications for methane budget**

**Methane varies by ± 50%**

- **Temp.**
- **CO₂**
- **CH₄**

![Graph showing temperature, CO₂, and CH₄ concentrations](image)

[Sowers and Bender, 1995]

**What drives glacial-interglacial variability in methane?**

**Wetland emissions?**
- Khalil and Rasmussen [1987]
- Crutzen and Brühl [1993]
- Chappellaz et al. [1993, 1997]
- Martinerie et al. [1995]
- Brook et al. [2000]
- Fischer et al. [2008]
- Singarayer et al. [2011]
- Levine et al. [2011a, 2011b]

**OH sink?**
- Kaplan [2002]
- Valdes et al. [2005]
- Kaplan et al. [2006]

<table>
<thead>
<tr>
<th>Decrease in LGM methane emissions</th>
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<tr>
<td>Murray et al. [2013]</td>
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<td>Weber et al. [2010]</td>
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<td>Kaplan et al. [2006]</td>
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(Implied from ΔLCH₄)

**Our static/increased methane lifetimes at LGM consistent with a higher role for wetland emissions**

**Implied source changes from LCH₄ consistent with previous bottom-up LGM emission estimates**

**Global methane lifetime against oxidation by tropospheric OH**

\[ \tau_{\text{CH}_4, \text{OH}} = \frac{\int_{\text{surface}}^\text{TOA} [\text{CH}_4] dM}{\int_{\text{surface}} k_{\text{CH}_4 + \text{OH}}(T) [\text{OH}][\text{CH}_4] dM} \]

- Can’t treat CH₄ distribution constant on glacial timescales; \( k_{\text{CH}_4 + \text{OH}} \) is not enough alone

**Decreases in integrated methane loss rate from [OH]↓ and T↓ attenuated by increases in tropical fraction of methane burden at LGM**

![Graph showing methane concentrations](image)

Kaplan et al. [2006]

- Preind
- LGM

We prescribe methane from ice cores; 33% higher fraction in tropics at LGM. Supported by methane emission models.
Chemical feedbacks on glacial cycles?

Next step: Put aerosols back into GCM and re-run to calculate radiative forcing (RF).

Large decrease in organic aerosol at LGM leads to regional warming, providing a negative feedback; comparable in magnitude to present-day inorganic RF.