Climate-driven changes in tropospheric oxidant abundances

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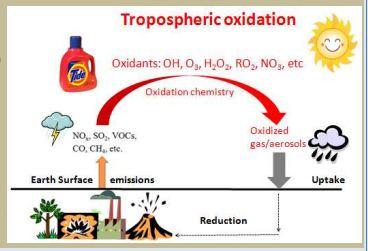
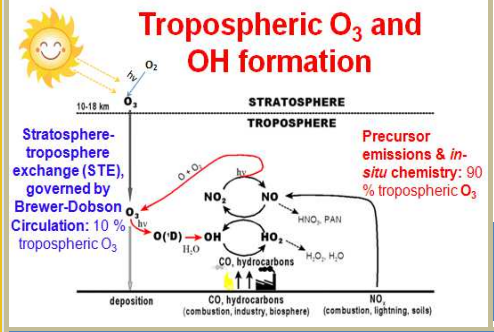
The tropospheric oxidation capacity

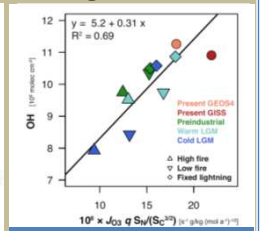
- The concentration of tropospheric oxidants (i.e., ozone (O_3) and OH) determine the lifetimes of reduced gases (CH_4, CO, VOCs) and the production of secondary aerosols, and determine the oxidation capacity of the atmosphere (*Thompson, 1992*).
- Knowledge of variability in the tropospheric oxidation capacity is important in terms of understanding the variations in atmospheric short-lived climate-forcing pollutants.



How does the tropospheric oxidation capacity vary with climate?

Oxidant cycling and influencing factors

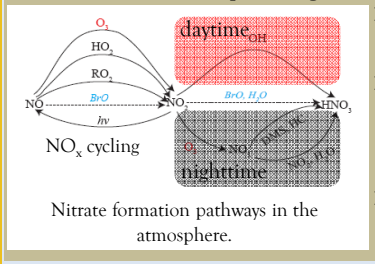




Tropospheric OH is most sensitive to surface UV-B levels, water vapor, and lightning (*Murray et al., 2014*)

In-situ chemistry and climate dynamics (STE) both influence tropospheric ozone

An ice-core proxy of oxidants: $\Delta^{17}O(NO_3^-)$

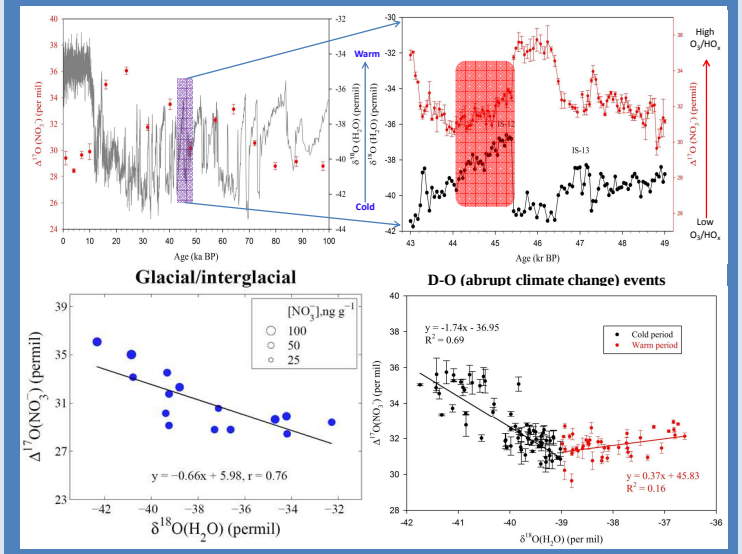


Nitrate formation pathways in the atmosphere.

- Oxidants are chemically active and there is a lack of long records to determine their past variability with climate;
- $\Delta^{17}O(NO_3^-)$ reflects the O_3/HO_x ratio at the time of nitrate formation, with higher O_3/HO_x ratios leading to larger $\Delta^{17}O(NO_3^-)$, due to the high $\Delta^{17}O$ values in ozone (35 ‰) vs. other oxidants (0 ‰);
- The preservation of nitrate in polar ice sheets renders $\Delta^{17}O(NO_3^-)$ a proxy to assess past variations in tropospheric oxidants;

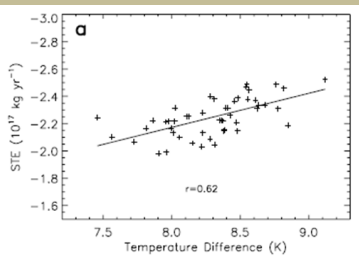
We define the A-value to represent the effect of O_3/HO_x ratio change on $\Delta^{17}O(NO_3^-)$, where $A = \frac{k_{R1}[NO][O_3]}{k_{R1}[NO][O_3] + k_{R2}[NO][HO_2] + k_{R3}[NO][RO_2]}$ (*Alexander et al., 2009*).

Greenland records of $\Delta^{17}O(NO_3^-)$

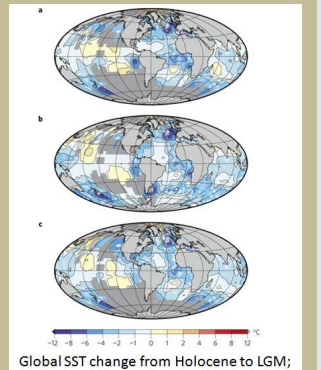


- $\delta^{18}O(H_2O)$ is a temperature indicator, and is larger in warmer climates;
- **Two-regime hypothesis**: 1) *in-situ* chemistry dominates tropospheric ozone variability in relatively warm climates; 2) STE dominates polar, tropospheric ozone variability in colder climates.

Response of STE to climate change



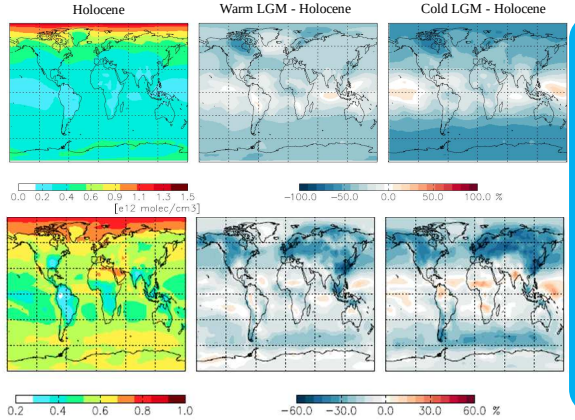
Modeled correlation of annual extra-tropical STE with the difference of sea-surface temperature (SST) between the tropics and extra-tropics in the Northern Hemisphere (*Olsen et al., 2007*).



Global SST change from Holocene to LGM; a: JJA; b: DJF; c: annual

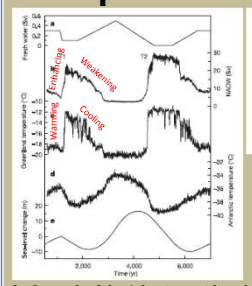
SST gradient between the tropics and the North Atlantic in the LGM was larger than in the Holocene (upper right, *MARGO Project Members*, 2009), suggesting enhanced glacial STE.

Response of *in-situ* chemistry to climate

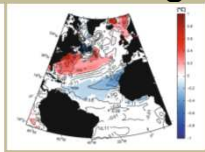


Changes in tropospheric O_3 (**Top**) and O_3/HO_x ratio (represented by the A-value) (**Bottom**) from the LGM to Holocene in the ICECAP model due to *in-situ* chemistry change only (*Murray et al.*, 2014).

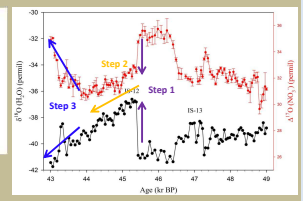
Rapid Climate Change and Oxidants



b: Strength of the Atlantic meridional overturning circulation (AMOC); **c**: Greenland temperature, its warming/cooling is controlled by the AMOC (*Knutti et al. 2004*).



A stronger AMOC leads to reduced SST gradient (*Persechino et al. 2012*).



Three step changes in climate and oxidants in a D-O cycle:
1. Abrupt warming: AMOC strengthens → reduced SST gradient → weakened STE → lower O_3/HO_x and $\Delta^{17}O(NO_3^-)$ in polar NH;
2. Gradual cooling: lower emissions of temperature-dependent O_3 precursurs → lower O_3/HO_x and $\Delta^{17}O(NO_3^-)$;
3. Abrupt cooling: AMOC weakens → enhanced SST gradient → enhanced STE → higher polar NH O_3/HO_x and $\Delta^{17}O(NO_3^-)$.

Conclusions and implications

- Mid- to high-northern latitude glacial O_3/HO_x ratio is higher than in the Holocene;
- Hypothesis: two regimes of climate control on tropospheric O_3 in the mid- to high-northern latitudes: 1) in cold climate, STE dominates; 2) in warm climate, *in-situ* chemistry dominates; At abrupt warming/cooling, STE change leads to rapid changes in O_3/HO_x ratio;
- The rapid STE change implies variations in Brewer-Dobson circulation over climate transitions, which alters stratospheric ozone distribution and thus UV-B radiation on the earth's surface, impacting global tropospheric OH and the oxidation capacity.

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