Photo by Rob Kerr

Ozone enhancement in Western U.S. wildfire plumes at the Mt. Bachelor Observatory: The Role of NOx

Pao Baylon, University of Washington, 18 June 2014

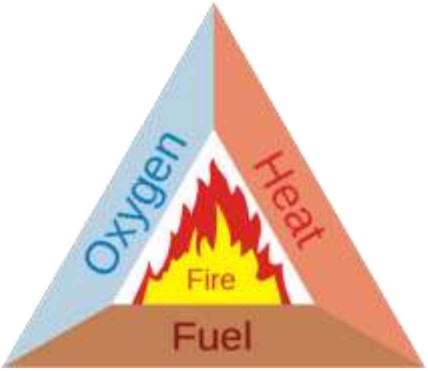
Outline

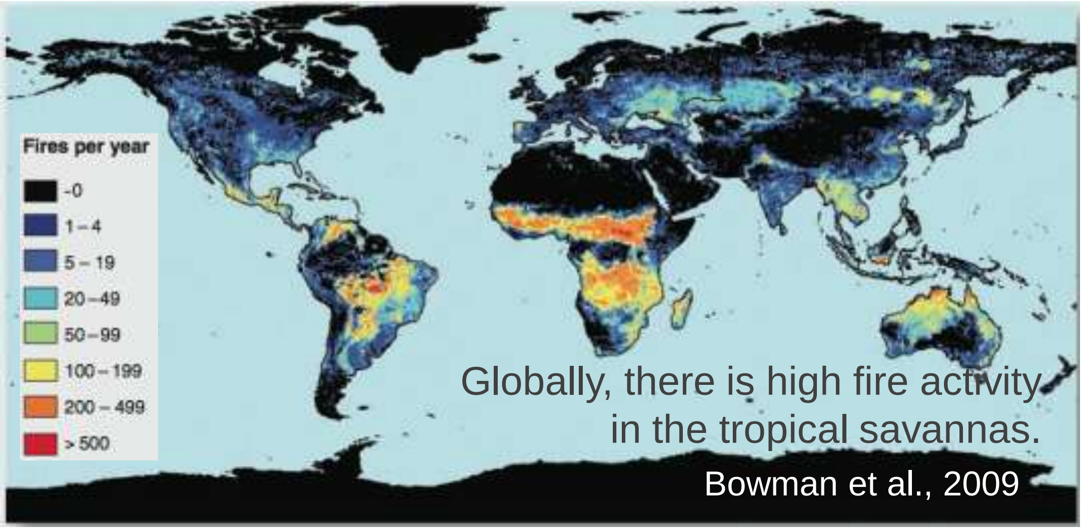
- Wildfire chemistry
- O_3 enhancement in Summer 2012 and 2013 individual wildfire plumes at MBO
- Case studies

1. Wildfire chemistry

Fire ingredients: “Fire triangle”

- Three components needed for **ignition and combustion** to occur: **fuel**, **oxygen** and **heat**
- Take away one of the three = **control and extinguish** the fire
- Wildfires usually ignited by **heat from the sun** or by **lightning**
- Direct negative effects: **smoke pollution**, **ecosystem degradation**, **human health impacts**





Globally, there is high fire activity in the tropical savannas.

Bowman et al., 2009

Adapted from Wiedinmyer 2014

Greenhouse Gases
Hydrocarbons
Oxygenated Compounds
Nitrogen-Containing Compounds
Sulfur-Containing Compounds
Halogen-Containing Compounds
Particulates

Carbon Dioxide (CO_2)	2-Methyl-1-Pentene (C_6H_{12})	Nitric Oxide (NO)
Methane (CH_4)	*n*-Hexane (C_6H_{14})	Nitrogen Dioxide (NO_2)
Hydrogen (H_2)	Heptane (C_7H_{16})	Nitrous Acid (HONO)
Carbon Monoxide (CO)	Benzene (C_6H_6)	Methyl Nitrate ($MeONO_2$)
Acetylene (C_2H_2)	Toluene ($C_6H_5CH_3$)	Ammonia (NH_3)
Ethylene (C_2H_4)	Xylenes	Hydrogen Cyanide (HCN)
Ethane (C_2H_6)	Ethylbenzene (C_8H_{10})	Acetonitrile (CH_3CN)
Propadiene (C_3H_4)	Methanol (CH_3OH)	Propenenitrile (C_3H_3N)
Propylene (C_3H_6)	Phenol (C_6H_5OH)	Propanenitrile (C_3H_5N)
Propane (C_3H_8)	Formaldehyde (HCHO)	Pyrrole (C_4H_5N)
1-Butene (C_4H_8)	Glycolaldehyde ($C_2H_4O_2$)	Carbonyl Sulfide (OCS)
1,3 Butadiene (C_4H_6)	Acetaldehyde (CH_3CHO)	Dimethyl Sulfide (C_2H_6S)
trans-2-Butene (C_4H_8)	Propanal (C_3H_6O)	Sulfur Dioxide (SO_2)
n-Butane (C_4H_{10})	Hexanal ($C_6H_{12}O$)	Methyl Bromide (CH_3Br)
i-Butane (C_4H_{10})	Acetone (C_3H_6O)	Methyl Iodide (CH_3I)
trans-2-Pentene (C_5H_{10})	Methacrolein (C_4H_6O)	Trichloromethane ($CHCl_3$)
cis-2-Pentene (C_5H_{10})	Crotonaldehyde (C_4H_6O)	OC
n-Pentane (C_5H_{12})	Methyl Vinyl Ketone (C_4H_6O)	BC
i-Pentane (C_5H_{12})	3-Pentanone ($C_5H_{10}O$)	Total PM
3-Methyl-1-Butene (C_5H_{10})	Furan (C_4H_4O)	Total Particulate Carbon
Isoprene (C_5H_8)	Formic Acid (HCOOH)	$PM_{2.5}$
Cyclopentane (C_5H_{10})	Acetic Acid (CH_3COOH)	PM_{10}

Key ingredients for **ozone production**:

VOCs
OVOCs
NOx

$$\text{VOCs, OVOCs, NOx} \xrightarrow{\text{sunlight}} O_3$$

But why do some wildfires produce O_3 while others do not?

$\Delta O_3/\Delta CO$ depends on biome and transport time

- $\Delta O_3/\Delta CO$ tends to **increase** with plume age.
- Equatorial regions tend to have **significantly greater** $\Delta O_3/\Delta CO$.

Boreal/Temperate:

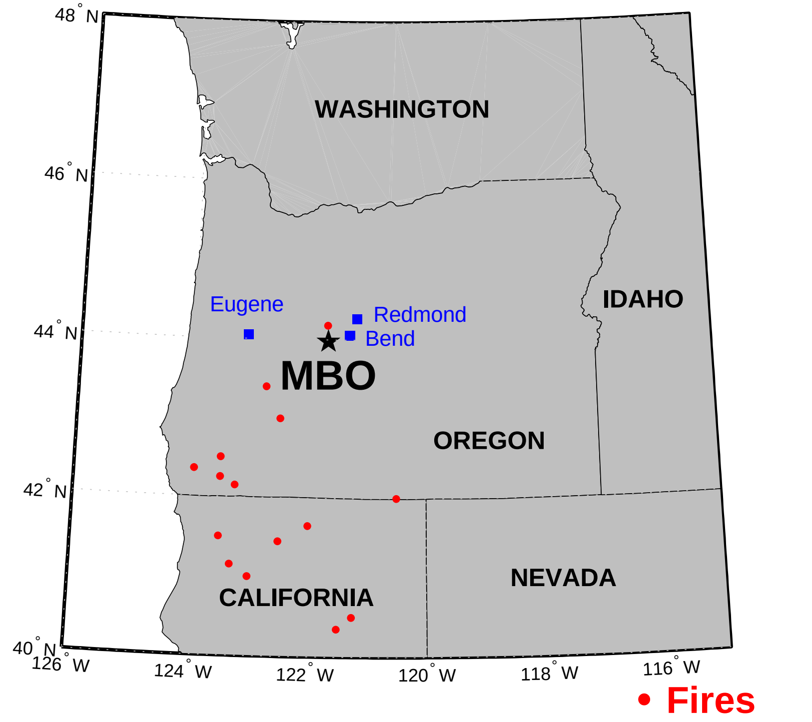
Plume Age	Mean $\Delta O_3/\Delta CO$ (ppbv/ ppbv) (no. of plumes)	Range of $\Delta O_3/\Delta CO$ (ppbv/ppbv)
≤ 1-2 days	0.018 (n=55)	-0.032 – 0.34
2-5 days	0.15 (n=39)	-0.07 – 0.66
≥ 5 days	0.22 (n=29)	-0.42 – 0.93

Tropical/Subtropical:

Plume Age	Mean $\Delta O_3/\Delta CO$ (ppbv/ ppbv) (no. of plumes)	Range of $\Delta O_3/\Delta CO$ (ppbv/ppbv)
≤ 1-2 days	0.14 (n=59)	-0.06 – 0.37
2-5 days	0.35 (n=13)	0.26 – 0.42
≥ 5 days	0.63 (n=18)	0.19 – 0.87

Jaffe and Wigder, 2012

Mt. Bachelor Observatory



Research site atop a dormant volcano (2.7 km a.s.l.) in **central Oregon** established in 2004

CO, **O_3**, Mercury, PM, meteorological parameters

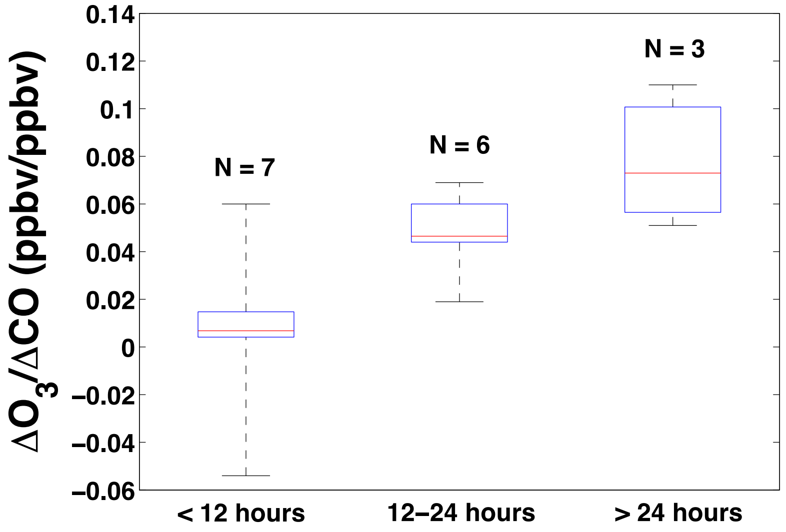
2012 fire season: added CO_2, **NOx**, **NOy**, EC/OC

2013 fire season: added **PAN** to 2012 measurements

2. O_3 production from individual plumes

There were a total of 19 events observed at MBO during Summer 2012 and 2013.

15 events with **O_3 enhancement**
1 event with **O_3 loss**
3 events with **no O_3 enhancement/loss**



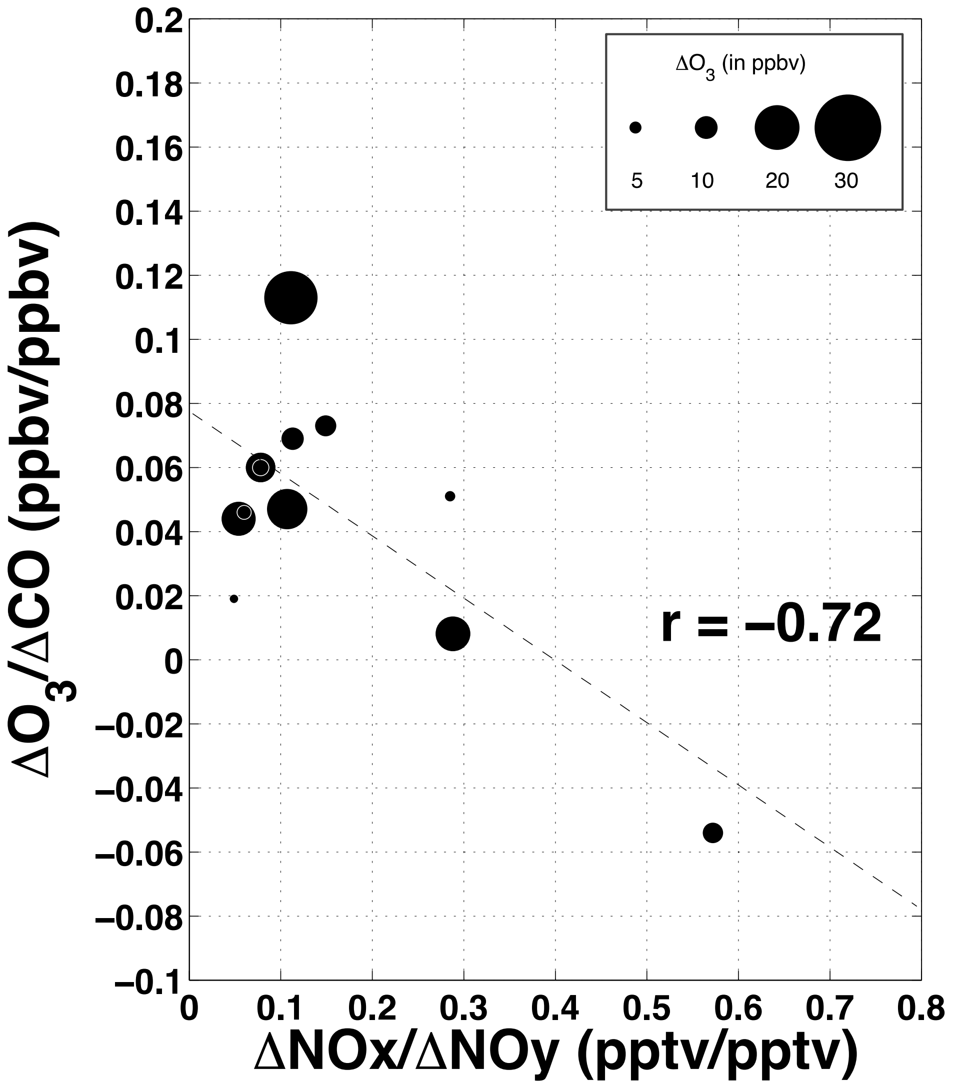
$\Delta O_3/\Delta CO$ **increases** with transport time.

Strong, negative correlation between $\Delta O_3/\Delta CO$ and $\Delta NOx/\Delta NOy$ enhancement ratios.

Degree of oxidation is therefore a key factor for O_3 production.

Size of markers proportional to **absolute ozone enhancement ΔO_3**.

Even though $\Delta O_3/\Delta CO$ is low, the **ΔO_3 may not be so low** (due to high CO enhancements).



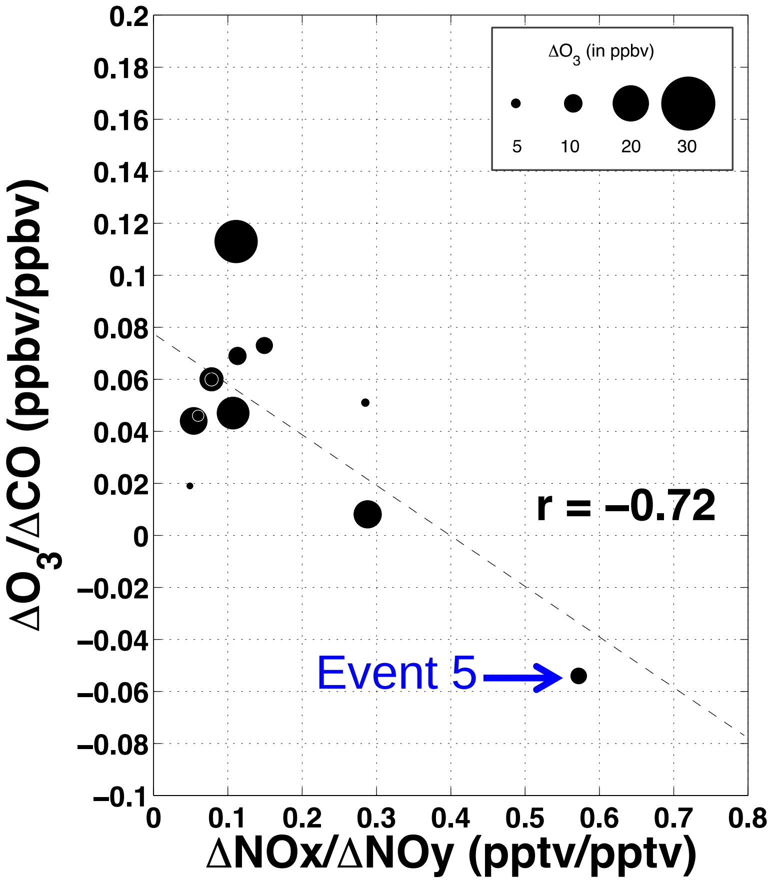
What about events **without** ozone enhancement/loss?

- **3** events belong to this category.
- **2** of them have the **highest water vapor enhancements**, +2.41 and +2.52 g/kg, which indicate a BL influence and loss of O_3 via dry deposition as it was transported to MBO.
- All **3** events are also associated with relatively **small ΔNOy/ΔCO ratios**, which suggests that NOx emissions may have not been high enough to allow O_3 enhancement.
- **1** event was observed during **nighttime**, which suggests minimal photochemistry during transport.

3. Case studies

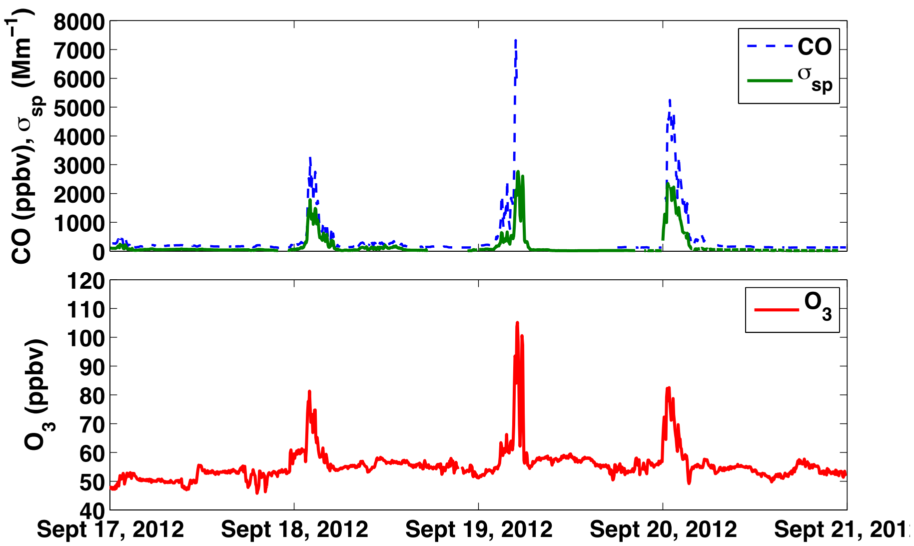
Case study: O_3 loss (Event 5)

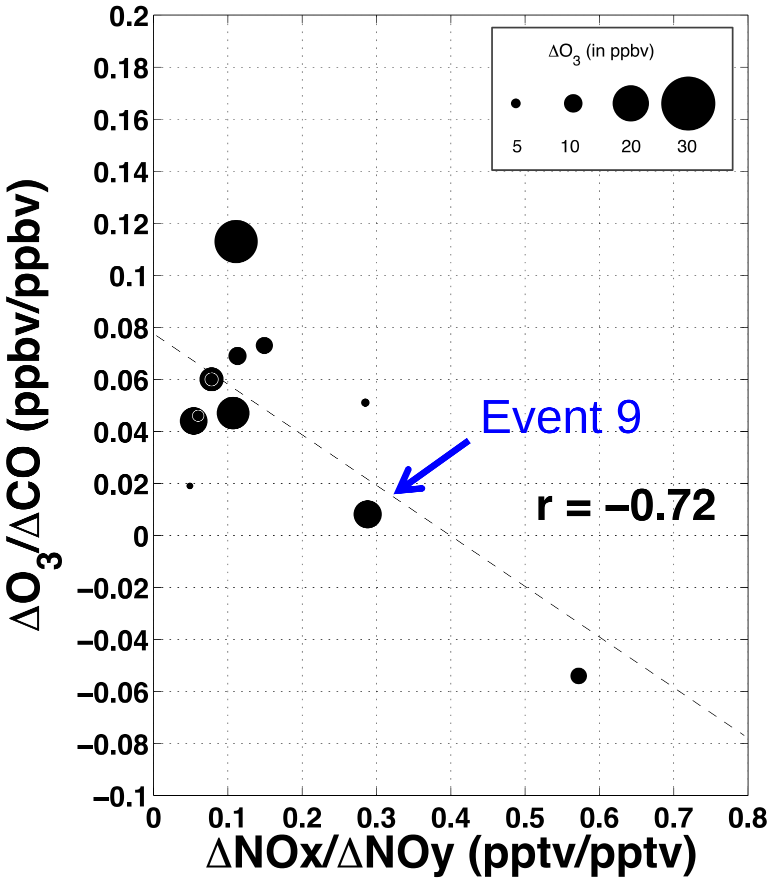
- Origin: NW California (transport time: 12 hours)
- High ΔNOx/ΔNOy ratio of 0.57 indicates a **fresh plume** that has undergone relatively little chemical processing.
- O_3 loss due to **nighttime chemistry** (maximum σ_{sp} and CO observed on Aug 27 3:25 local time)



Case study: Pole Creek Fire

- Origin: 20 km north of MBO





Case study: Pole Creek Fire

View of Pole Creek smoke plume from Scott Pass 9/9/12

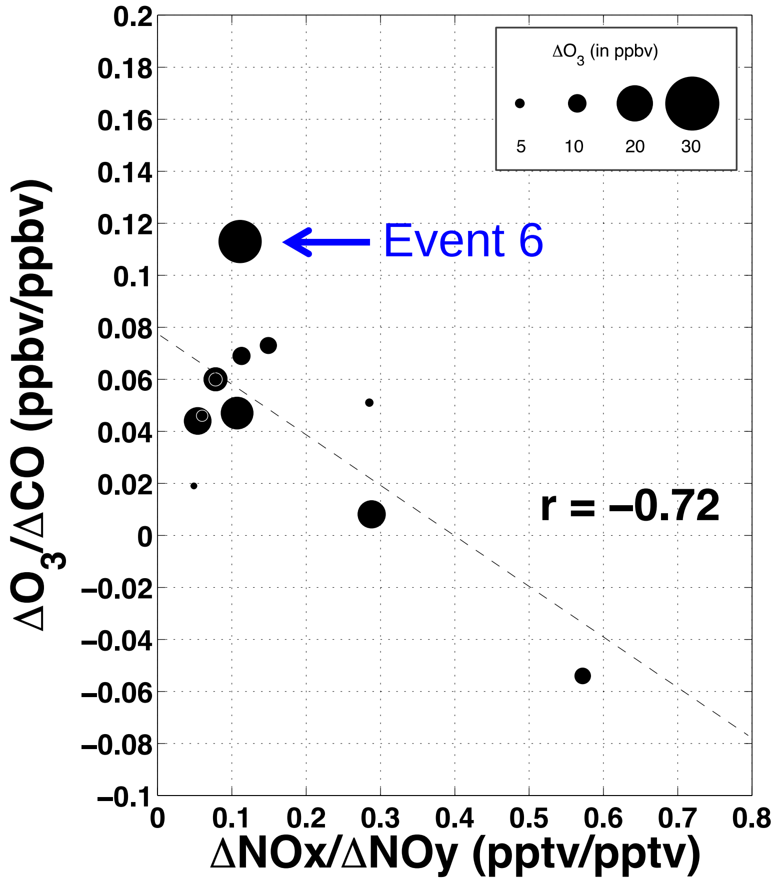
Credit: Rebecca Nore

View of Pole Creek smoke plume

View of Pole Creek fire plume from MBO taken on 9/18/12
Credit: Jonathan Hee

Case study: O_3 enhancement (Event 6)

- Origin: N California (transport time: 24-36 hours)
- Fire plume exhibits all of the necessary characteristics for O_3 production:
  - **enhanced** ΔNOy/ΔCO
  - **daytime** exposure to sunlight
  - **low** ΔNOx/ΔNOy
  - **free tropospheric** transport



Summary

- $\Delta O_3/\Delta CO$ for the 2012 and 2013 fire plumes tends to **increase with source distance**.
- There is a **negative relationship** between $\Delta O_3/\Delta CO$ and $\Delta NOx/\Delta NOy$ ($r = -0.72$). This tells us that the **degree of oxidation** is a key factor for ozone production.
- Even if $\Delta O_3/\Delta CO$ is low, **ΔO_3 may still be high** if CO enhancements are large.
- Events that are not associated with ozone enhancement/loss are either **BL-influenced**, associated with **low $\Delta NOy/\Delta CO$** ratios, and/or associated with **minimal photochemistry**.