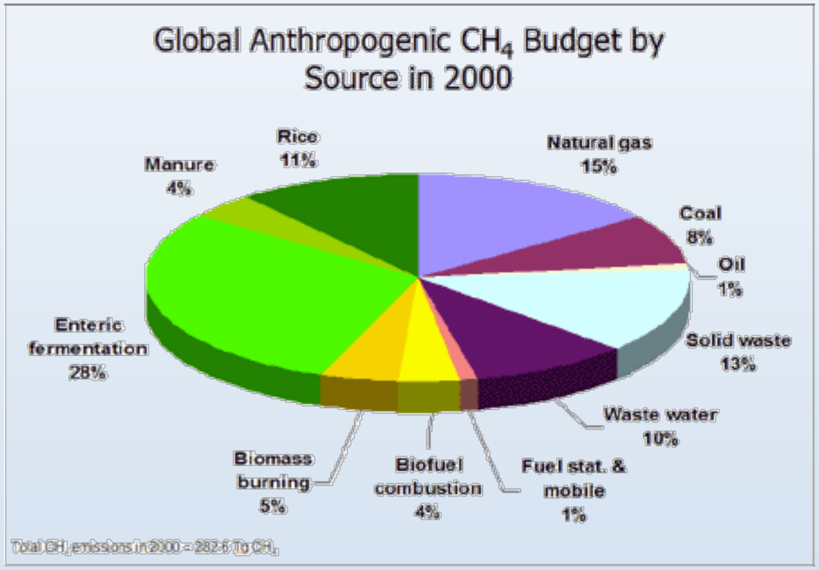
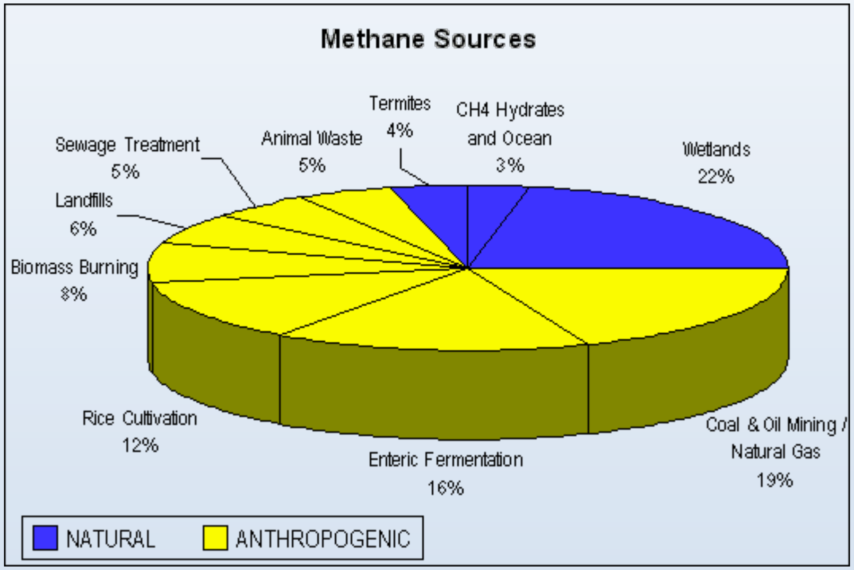
Atmospheric Chemistry

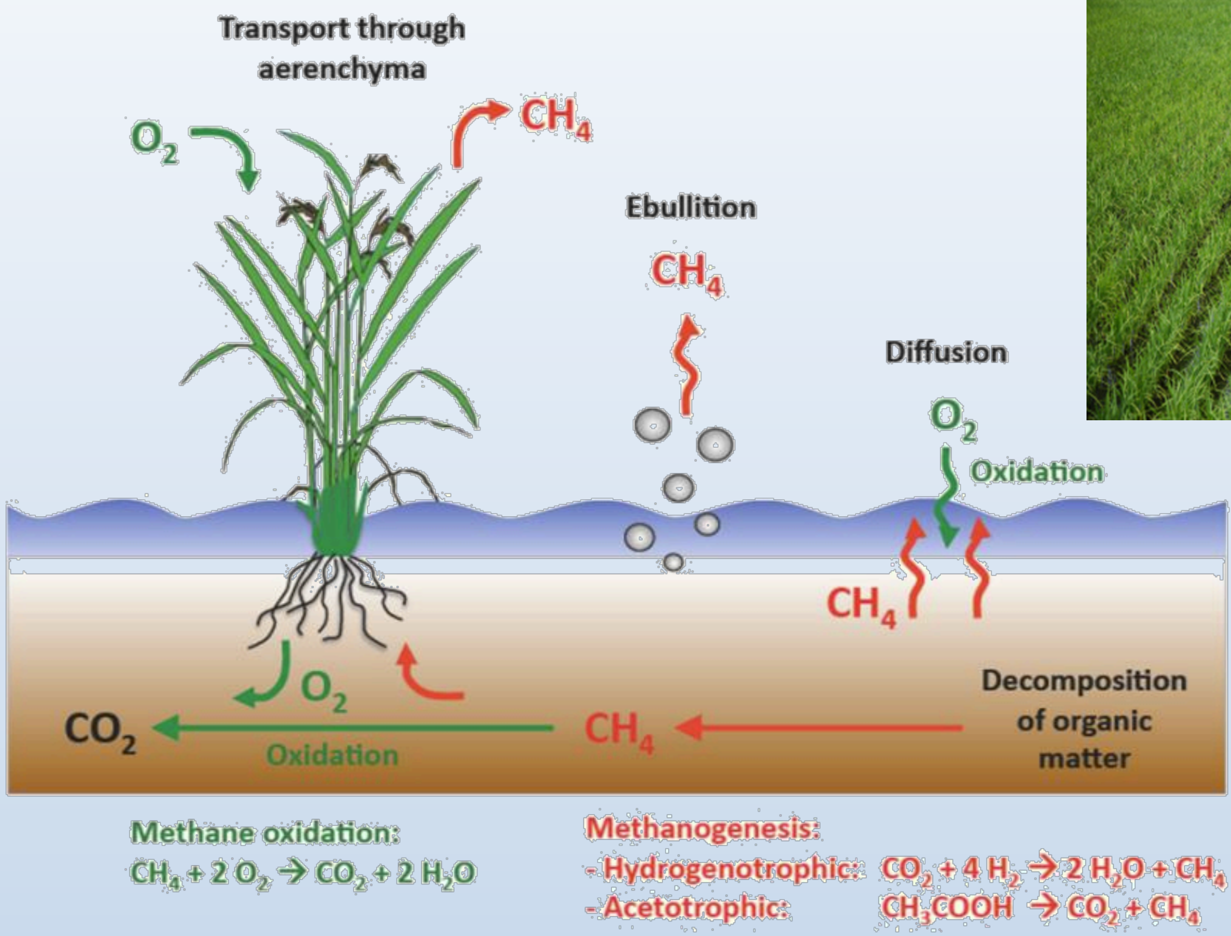
Lecture 15

Sources of Atmospheric Methane

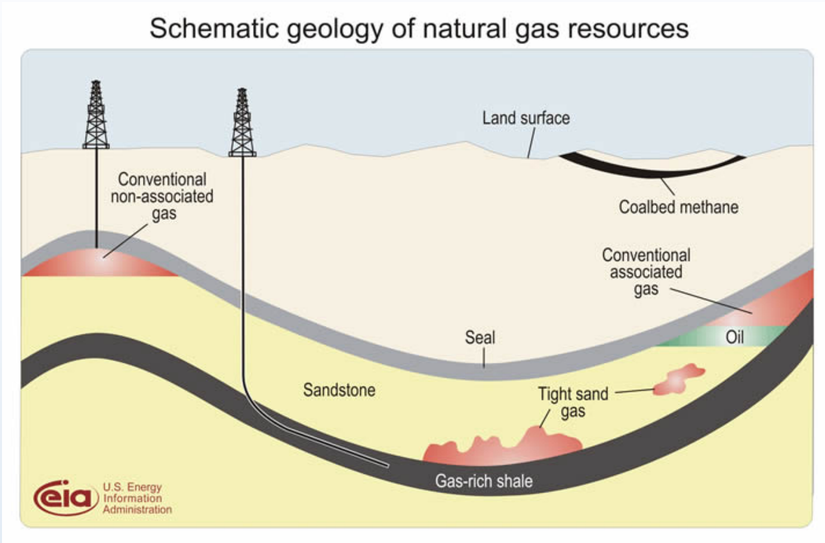




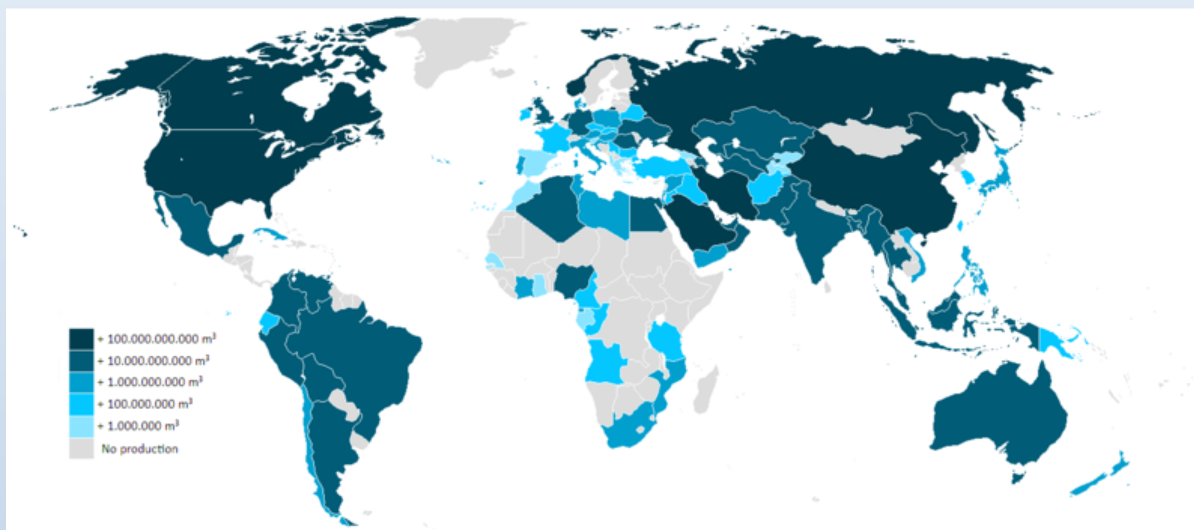
Methane is produced by anaerobic decomposition of organic matter



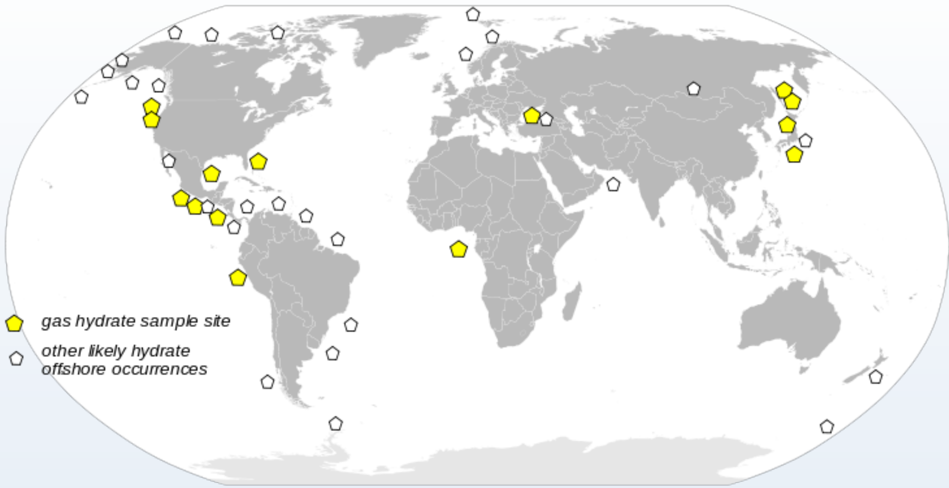
Flooded Rice Paddy

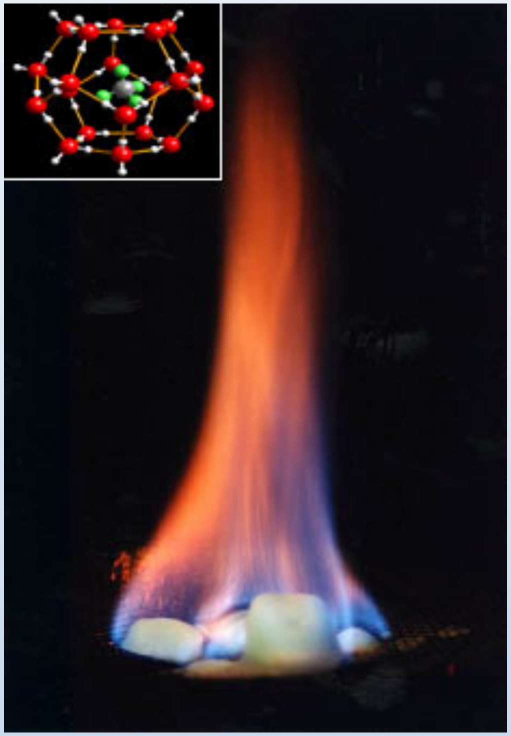


Sources of Methane: Natural Gas Deposits

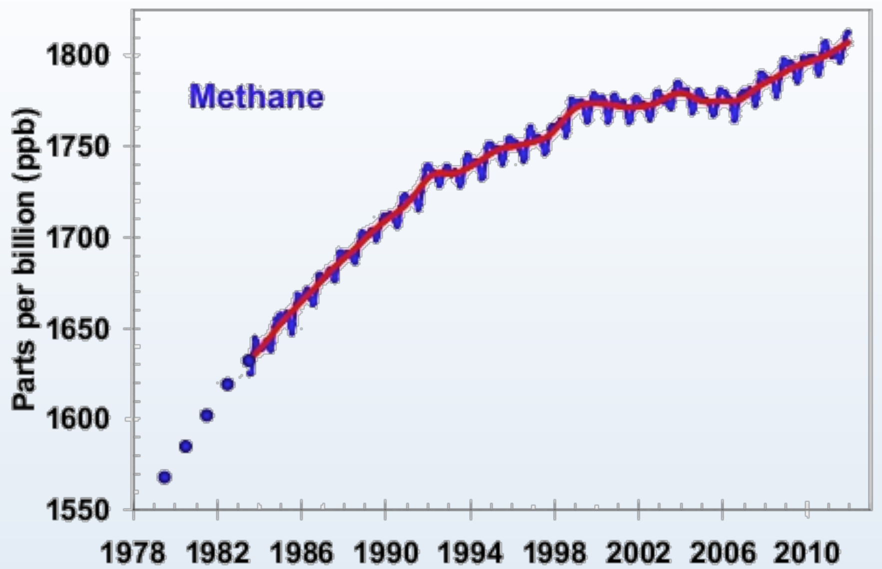


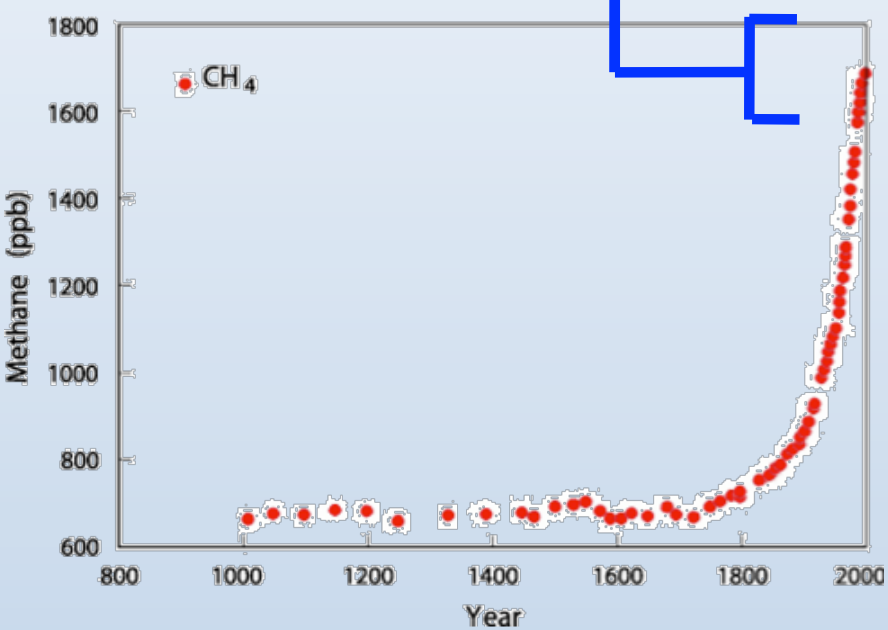
Sources of Methane: Clathrates or Natural Gas Hydrates

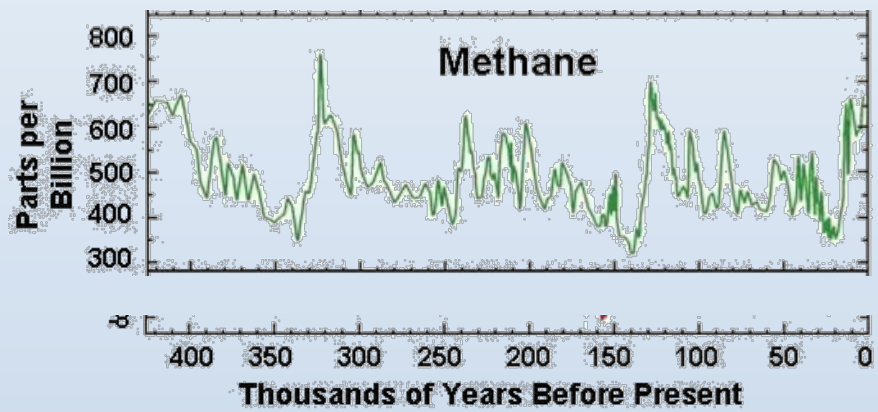




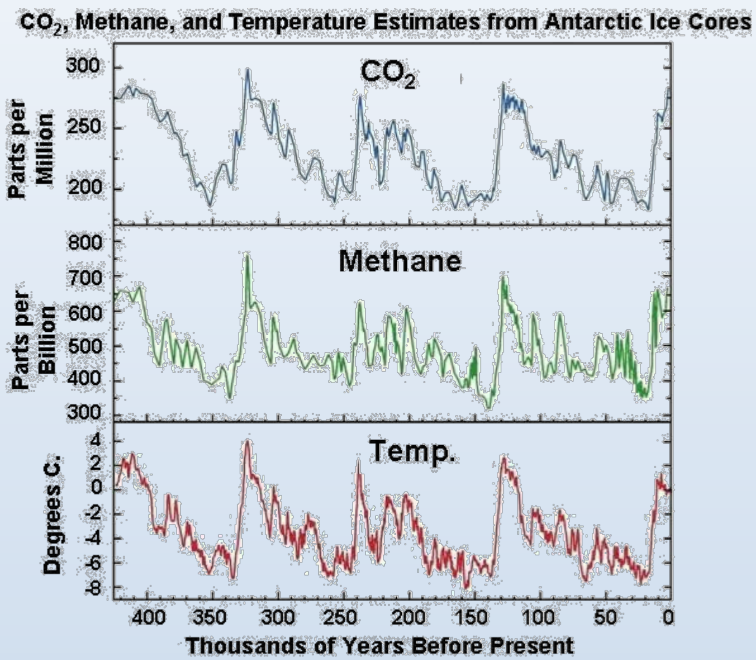
Atmospheric Methane History

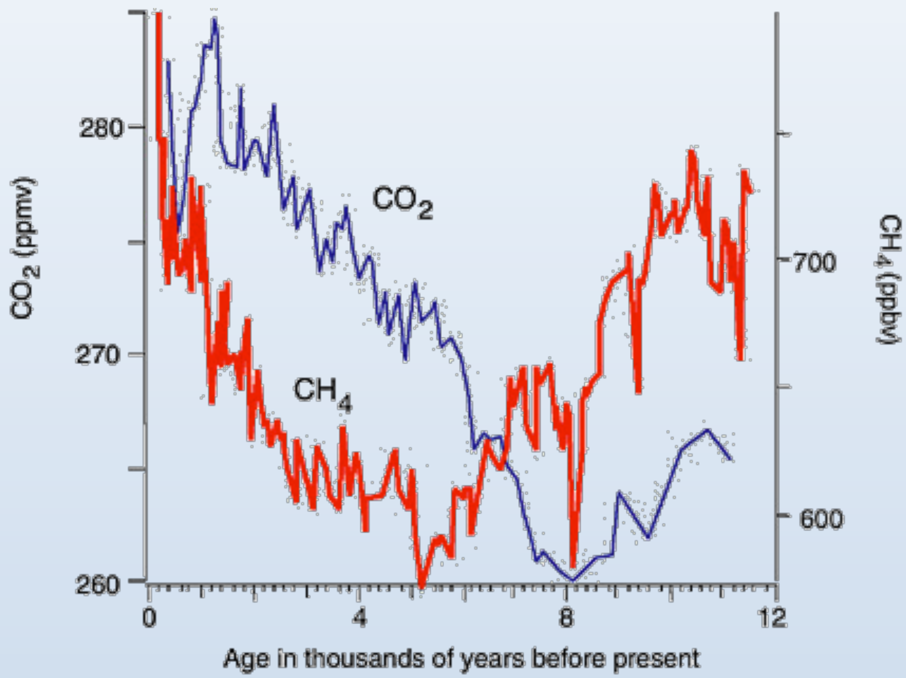


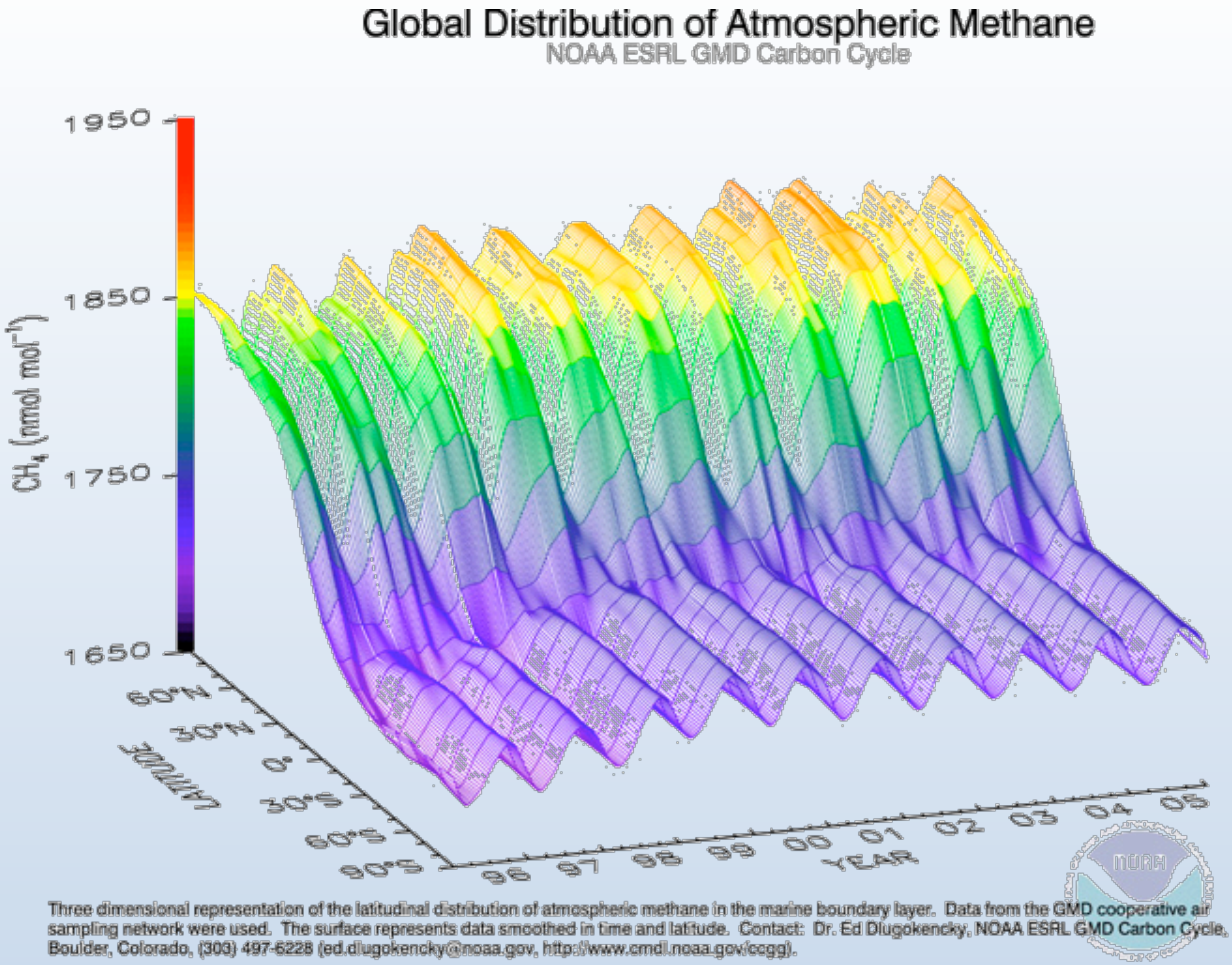




CO_2 and CH_4 exhibit similar behavior over ice-age time scales






Global Distribution of Atmospheric Methane
NOAA ESRL GMD Carbon Cycle
1950
1850
1750
1650
CH4 (nmol mol-1)
60°N
30°N
0°
30°S
60°S
90°S
LATITUDE
96
97
98
99
00
01
02
03
04
05
YEAR
Three dimensional representation of the latitudinal distribution of atmospheric methane in the marine boundary layer. Data from the GMD cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Contact: Dr. Ed Dlugokencky, NOAA ESRL GMD Carbon Cycle, Boulder, Colorado, (303) 497-6228 (ed.dlugokencky@noaa.gov, http://www.cmdl.noaa.gov/ccgg).

Basic Oxidation of Methane

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

But, CH_4 in a container with O_2 will not burn unless ignited

What starts the "burning" in the free atmosphere?

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

Hydrogen abstraction by the free radical OH

Methane Oxidation (continued)

Methyl radical adds an O_2 to make methyl peroxy

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

Two things can happen to methyl peroxy

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

or

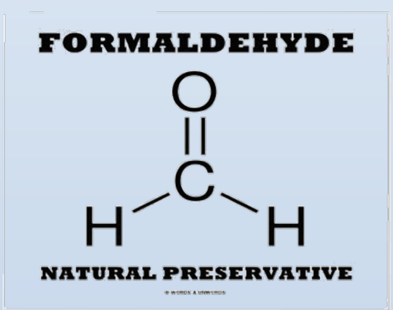
$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$

Methane Oxidation (continued)

Ignore second channel to CH_3OOH for the time being: CH_3O reacts rapidly with O_2 to lose another hydrogen atom

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

CH_2O is a relatively stable molecule, formaldehyde



Summarizing thus far

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$CH_4 + OH + 2O_2 + NO \rightarrow CH_2O + HO_2 + NO_2 + H_2O$$

What happens to formaldehyde?

Several pathways

Photolysis

$$CH_2O + h\nu \rightarrow CHO + H$$
$$CH_2O + h\nu \rightarrow CO + H_2$$

or reaction with OH

$$CH_2O + OH \rightarrow CHO + H_2O$$

CHO reacts with O_2 to form CO

$$CHO + O_2 \rightarrow CO + HO_2$$

Carbon monoxide, CO is a product of the oxidation of methane

All channels led to the formation of CO: depending on pathway, either H_2 was formed or 2 HO_2

CO the reacts with OH to form CO_2

$$CO + OH \rightarrow CO_2 + H$$

and we have completely oxidized the carbon atom

Summarizing the second part of the oxidation (from formaldehyde)

$CH_2O + h\nu \rightarrow CHO + H$

$CHO + O_2 \rightarrow CO + HO_2$

$CO + OH \rightarrow CO_2 + H$

2x: $H + O_2 + M \rightarrow HO_2 + M$

$CH_2O + 3O_2 + OH \rightarrow CO_2 + 3HO_2$

$CH_2O + OH \rightarrow CHO + H_2O$

$CHO + O_2 \rightarrow CO + HO_2$

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$CH_2O + 2O_2 + 2OH \rightarrow CO_2 + H_2O + 2HO_2$

$CH_2O + h\nu \rightarrow CO + H_2$

$CO + OH \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$CH_2O + O_2 + OH \rightarrow CO_2 + HO_2 + H_2$

The net HO_x formed will eventually combine via $OH + HO_2 \rightarrow H_2O + O_2$

What have we done?

$CH_4 + OH + 2O_2 + NO \rightarrow CH_2O + HO_2 + NO_2 + H_2O$

$CH_2O + 2O_2 + 2OH \rightarrow CO_2 + H_2O + 2HO_2$

$CH_4 + 4O_2 + 3OH + NO \rightarrow CO_2 + 2H_2O + 3HO_2 + NO_2$

Oxidized methane to CO_2 and $2H_2O$ plus used an extra 2 oxygen molecules to convert OH to HO_2 and NO to NO_2. Note that NO_2 photolyses easily to NO + O and the O atom forms ozone

What have we done?

$CH_4 + OH + 2O_2 + NO \rightarrow CH_2O + HO_2 + NO_2 + H_2O$

$CH_2O + O_2 + OH \rightarrow CO_2 + 3HO_2$

--

$CH_4 + 4O_2 + 2OH + NO \rightarrow CO_2 + H_2O + 4HO_2 + NO_2$

Oxidized CH_4 to CO_2 and one H_2O. Have created 2 HO_x that will eventually recombine to form the second H_2O. The NO_2 will photolyze to form O atoms and then ozone

What have we done?

$CH_4 + OH + 2O_2 + NO \rightarrow CH_2O + HO_2 + NO_2 + H_2O$

$CH_2O + O_2 + OH \rightarrow CO_2 + HO_2 + H_2$

$CH_4 + 3O_2 + 2OH + NO \rightarrow CO_2 + H_2O + H_2 + 2HO_2 + NO_2$

Oxidized CH_4 to CO_2 and one H_2O plus one H_2. Have converted 2OH to $2HO_2$. The NO_2 will photolyze to form O atoms and then ozone

What about the other channel for CH_3O_2 reaction?

$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$

This can be followed by

$CH_3OOH + h\nu \rightarrow CH_3O + OH$

which takes us back to the original chain reforming the O_2 that was used and converting HO_2 to OH, or it can be followed by

$CH_3OOH + OH \rightarrow CH_3O_2 + HO_2$

This second channel forms a catalytic cycle that converts HO_x back to H_2O

What about the other channel for CH_3O_2 reaction?

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$$
$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$$

$$HO_2 + OH \rightarrow H_2O + O_2$$

This HO_x destruction can counteract the HO_x production in one of the above steps. The net effect depends on the ratio of the reaction rate of CH_3O_2 with NO to that with HO_2 and depends on the ratio of photolysis rate of CH_3OOH to the reaction rate with OH.

Summarizing Methane Oxidation

- Produces CO_2 + $2H_2O$ with a minor channel that produces H_2 instead of the second H_2O
- Produces formaldehyde, CH_2O and carbon monoxide, CO as part of the degradation chain
- Can oxidize NO to NO_2 leading to O atom production and hence ozone production
- Can produce HO_x radicals or destroy them depending on conditions