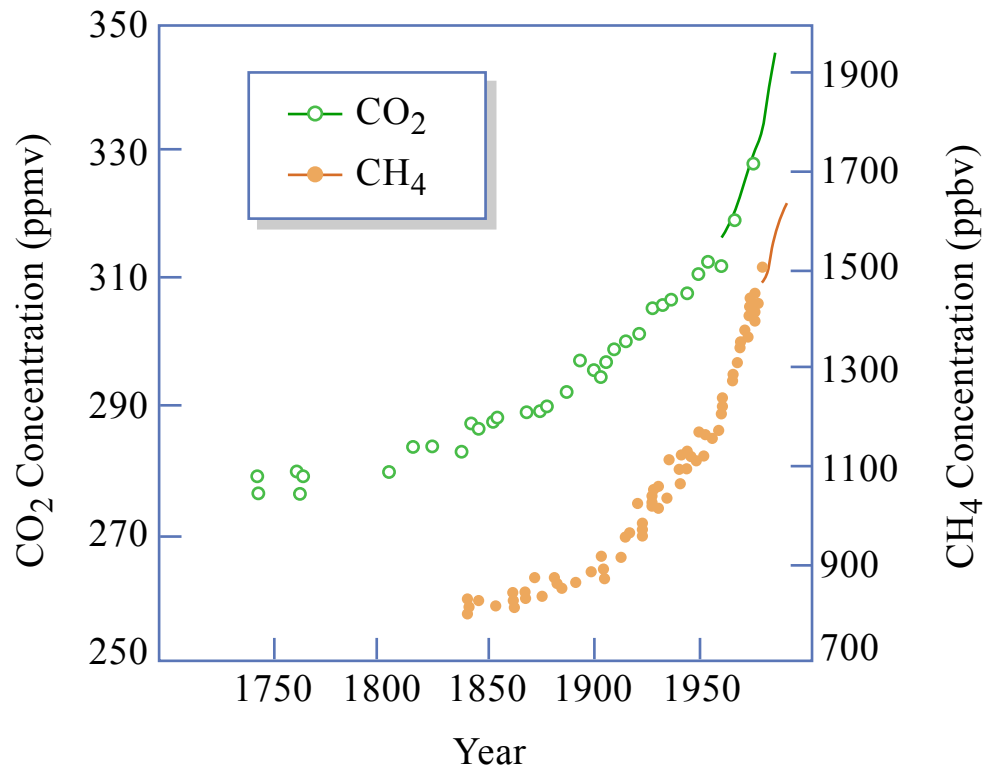


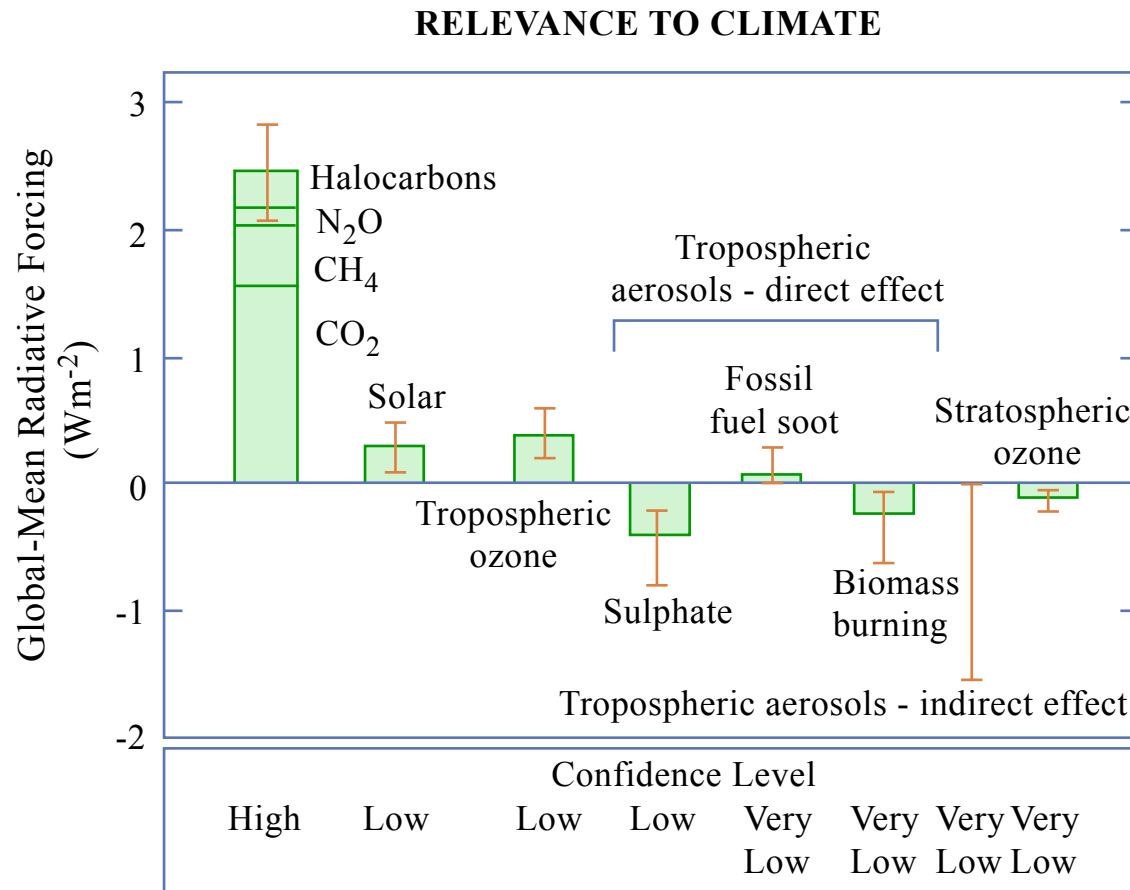
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Climate Physics and Chemistry
Fall 2006

Atmospheric Chemistry II:
Methane



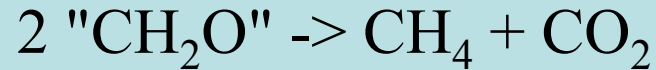
Reconstruction of the CO₂ and CH₄ increases since the preindustrial time from data, respectively, from the Siple (6) and DE08 (7) ice cores. Note the good agreement between the ice core data and the direct measurements (solid lines) in the atmosphere starting from 1958 (CO₂) and 1978 (CH₄).

Methane is a strong greenhouse gas and contributes to global warming



Estimates of the globally and annually averaged anthropogenic radiative forcing (in Wm^{-2}) due to changes in concentrations of greenhouse gases and aerosols from pre-industrial times to the present day and to natural changes in solar output from 1850 to the present day.

Main natural CH₄ source to atmosphere: anaerobic microbial fermentation in environments where all other oxidants (O₂, MnO₂, NO₃⁻, Fe₂O₃, SO₄⁼) are depleted:



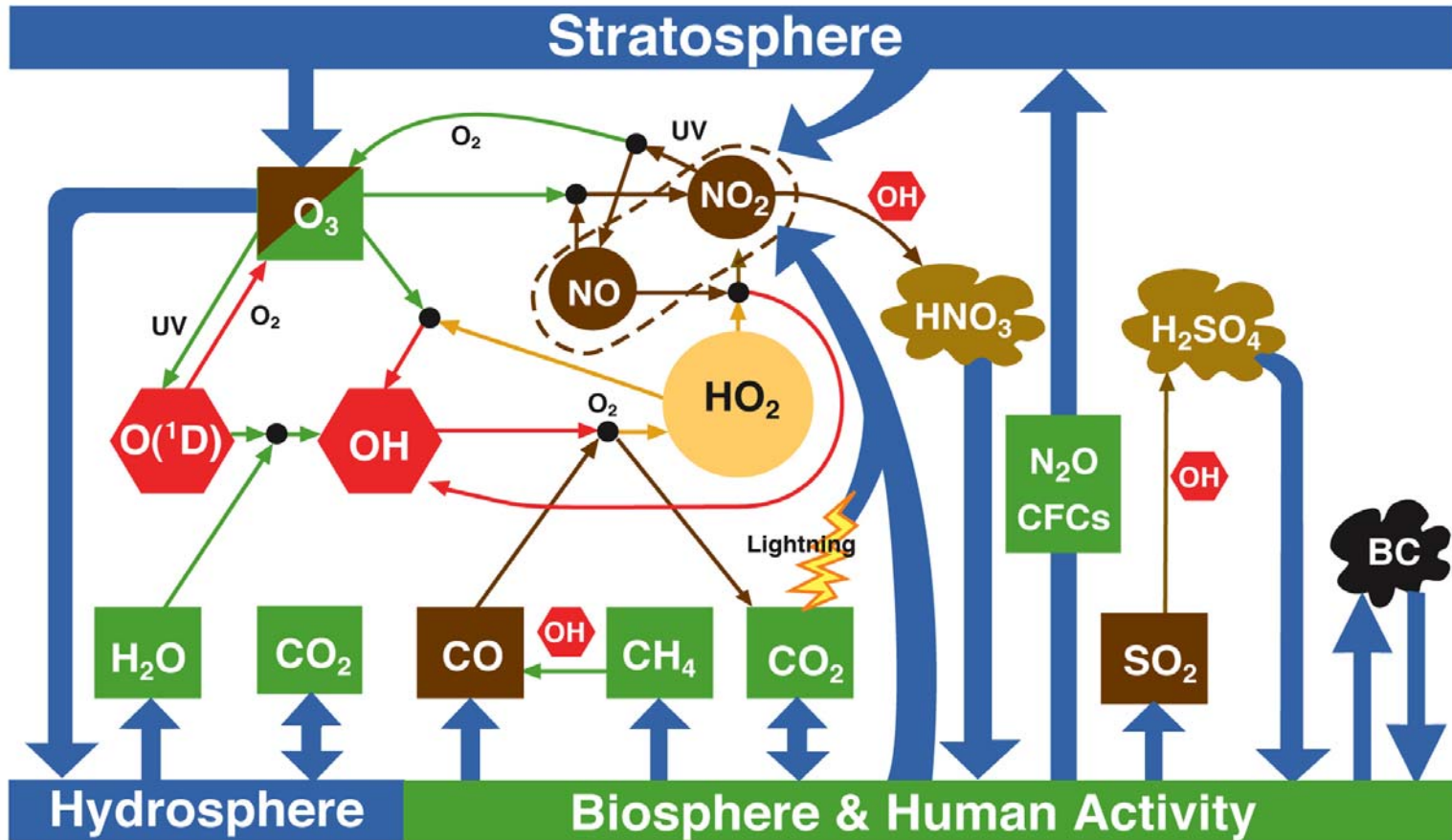
$\Delta G \sim -350$ kJ/mole of glucose

[actual direct precursors of CH₄ are fermentation of acetate and/or oxidation of hydrogen using CO₂ as the electron acceptor]

In some environments, this methane can escape into the oxic environment (e.g., gas bubbles rising through water). In other environments where transport goes through less reducing environments, methane can be lost by methanotropic bacteria. In marine sediments, CH₄ is consumed by the microbial reaction:



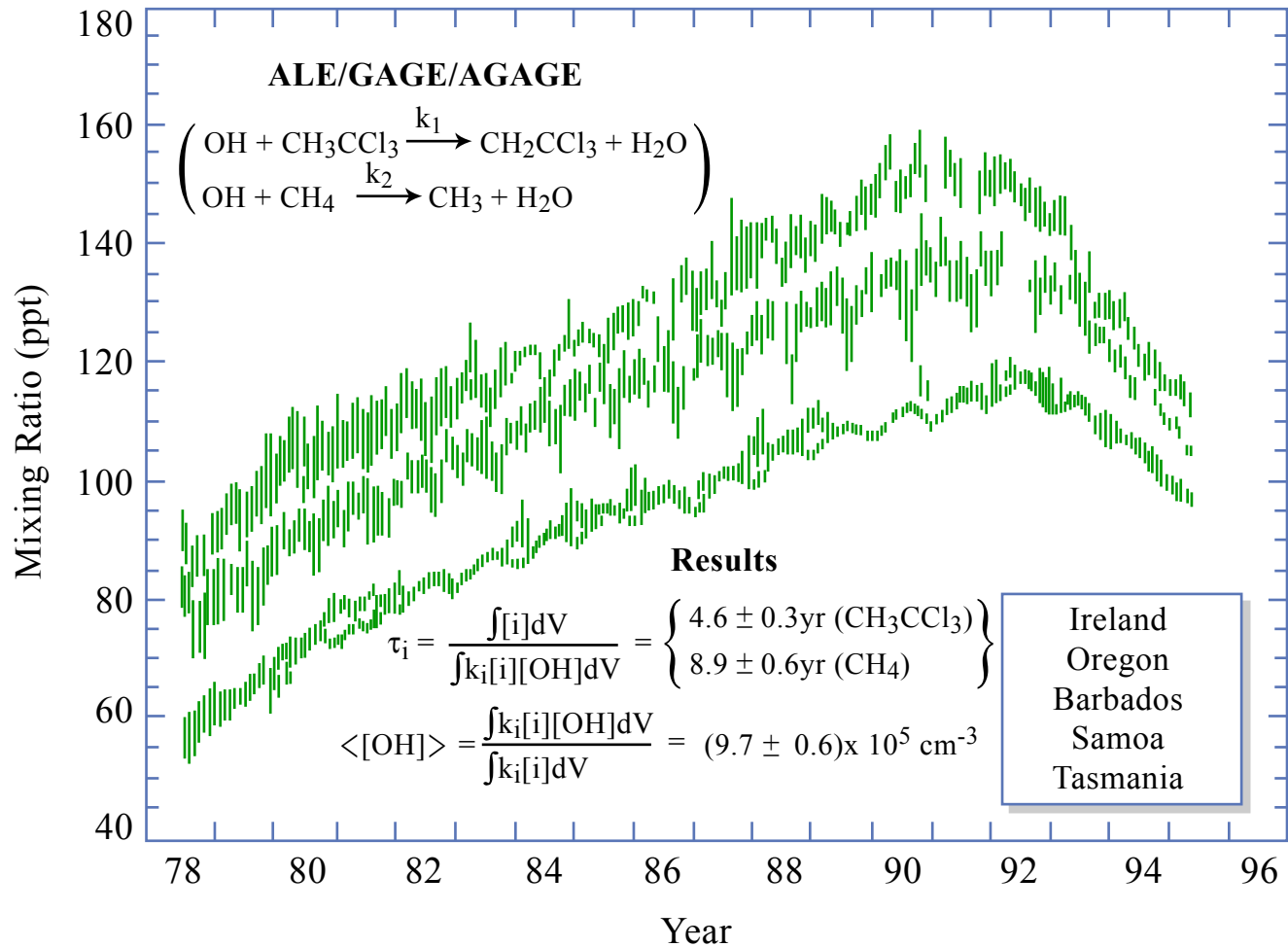
Interactions Between Air Pollution and Climate



Greenhouse Gases	Reactive Free Radical/Atom
Primary & Secondary Pollutants	Less Reactive Radicals
Absorbing Aerosols (BC)	Reflective Aerosols

Figure by MIT OCW.

CH3CCl3



Determination of OH by Inverse Method

Figure by MIT OCW. Adapted from Prinn, et al. *Science* 269 (1995): 187-192.

CH₄ sources:

- Some methane is emitted from the seafloor by natural gas seeps (major source of methane from this source is thermal cracking of buried organic matter) including “cold seeps” and “mud volcanos”. On some occasions methane can be emitted from methane hydrate decomposition. Usually, most this methane is oxidized before it is emitted to the atmosphere.
- CH₄ dominantly enters the atmosphere from land. The main natural sources are natural wetlands and termites. At present, these natural sources are supplemented by several anthropogenic sources – rice fields, enteric fermentation (cows), oil and natural gas leakage, coal mining, landfills, sewage, animal wastes, and biomass burning. Because most of the land is in the Northern Hemisphere, methane is slightly higher in the northern hemisphere, and maximum concentrations occur at high northern latitudes.

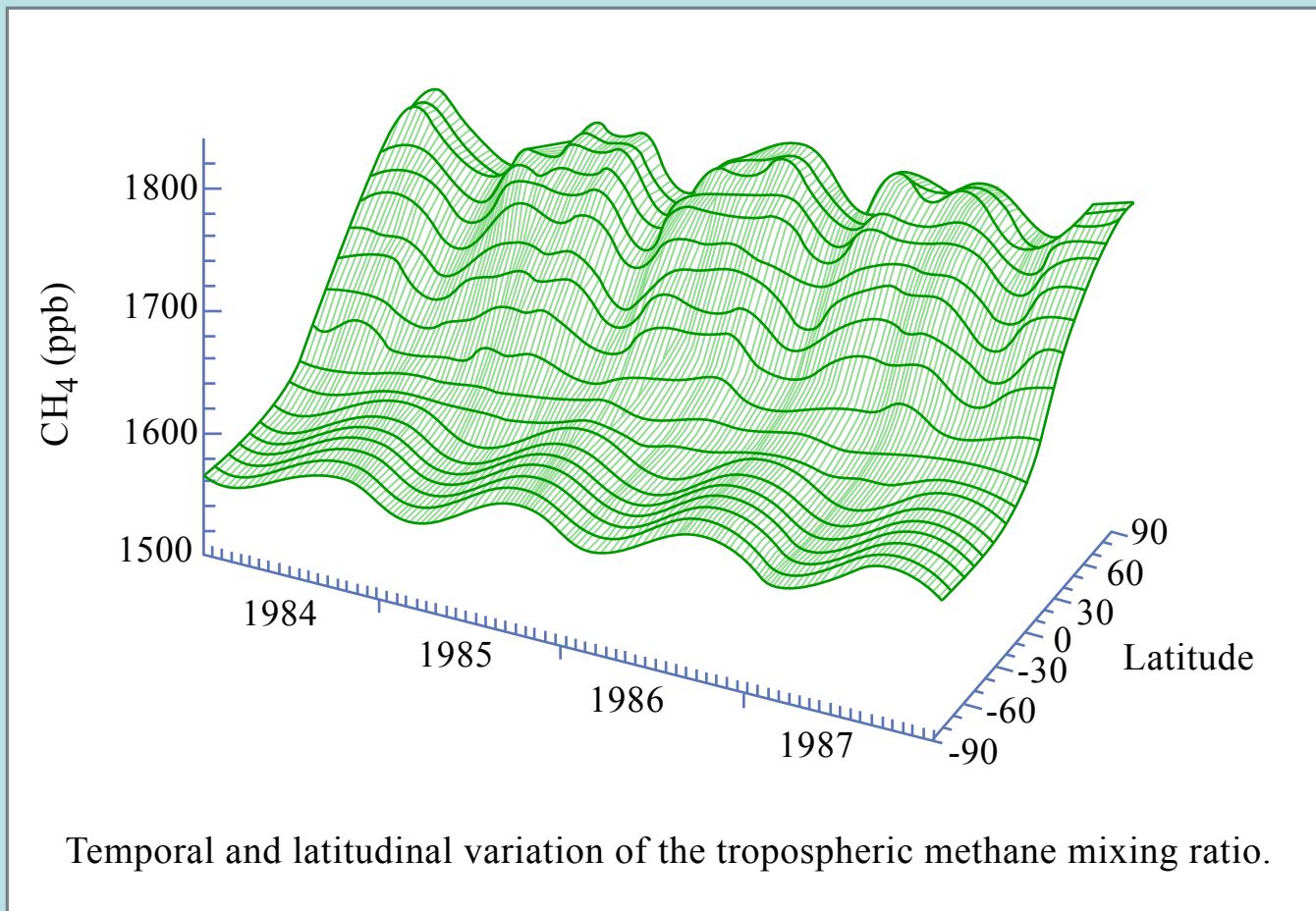
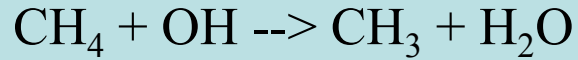


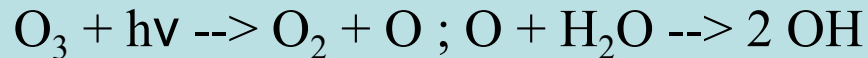
Figure by MIT OCW based on Fung, et al., 1991.

Methane Tropospheric Chemistry

- Main CH₄ tropospheric sink is reaction with OH radical:



- Tropospheric OH source is:



- OH is the main oxidizing molecule of the troposphere; it is involved in most tropospheric oxidation reactions. But its lifetime is short and its concentration is very low: $\sim 10^4$ atoms per cm³.
- "OH can react quickly with CO to yield CO₂, and with CH₄ and other hydrocarbons to form formaldehyde. In the process, OH is converted to HO₂ (hydroperoxyl), from which OH can be regenerated to start the chain all over again."

(Physics Today, Nov. 1996 p. 17)

- CH₄ tropospheric lifetime is ~ 8 yrs (best established through global model of anthropogenic methylchloroform CH₃CCl₄)

Methane has undergone large changes in the past due to climate modulation of methane sources

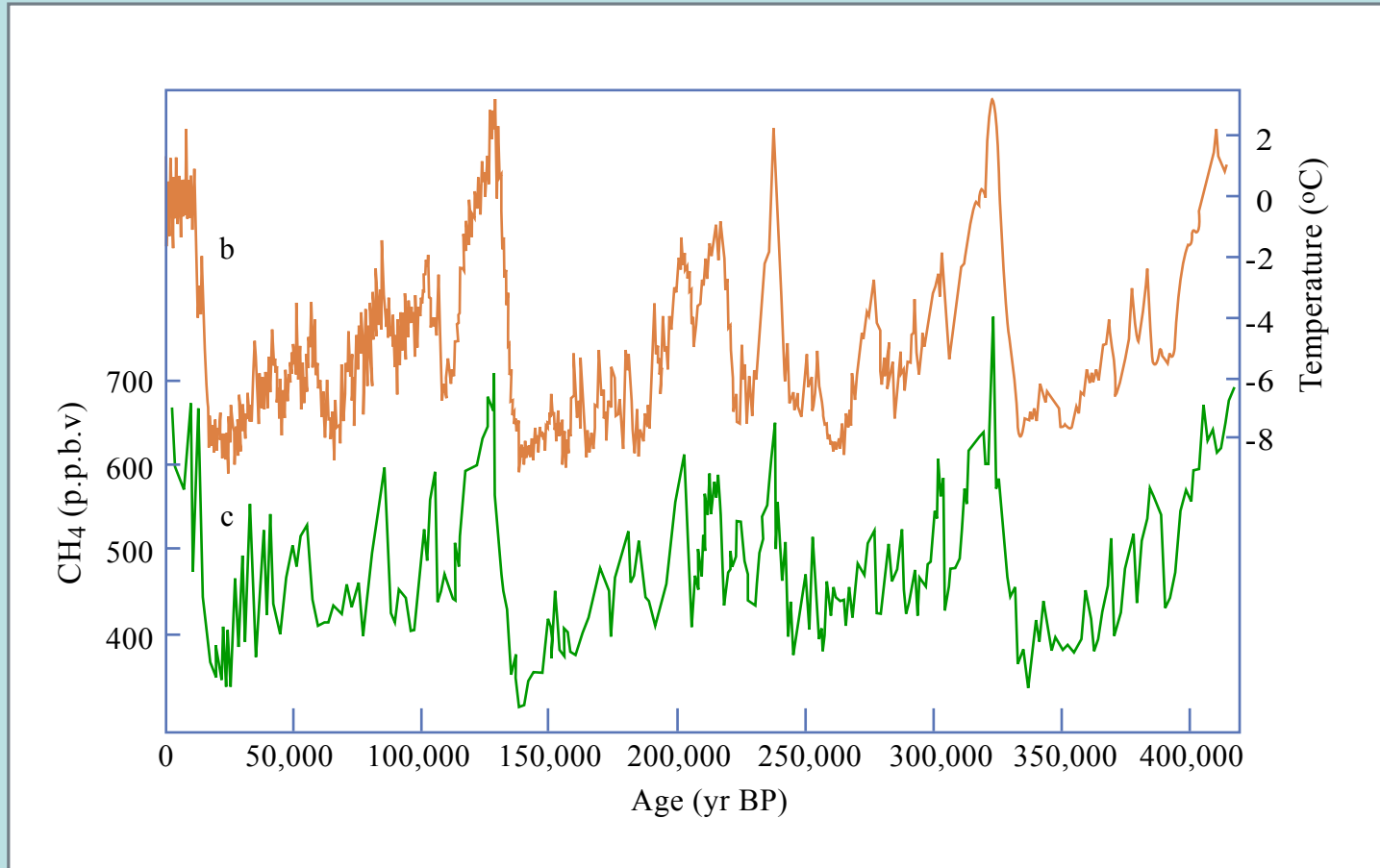


Figure by MIT OCW based on Nature Vol. 399, 1999.

Methane in the Vostok Ice Core

CH₄ budget

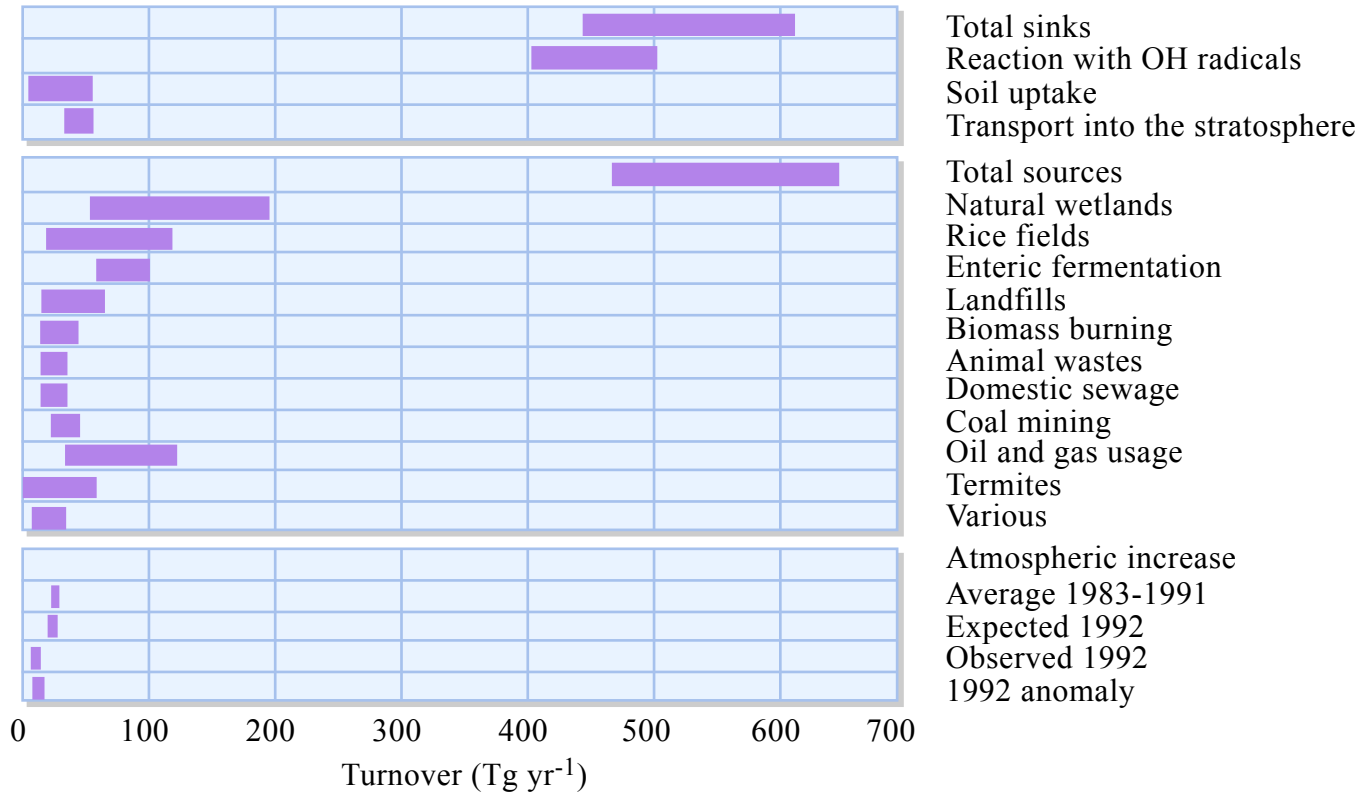


Figure by MIT OCW.

CH₄ budget

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Citation: see Table 4.2 IPCC report *Climate Change 2001: The Scientific Basis* on page 250.

Methane during the past 12,000 years

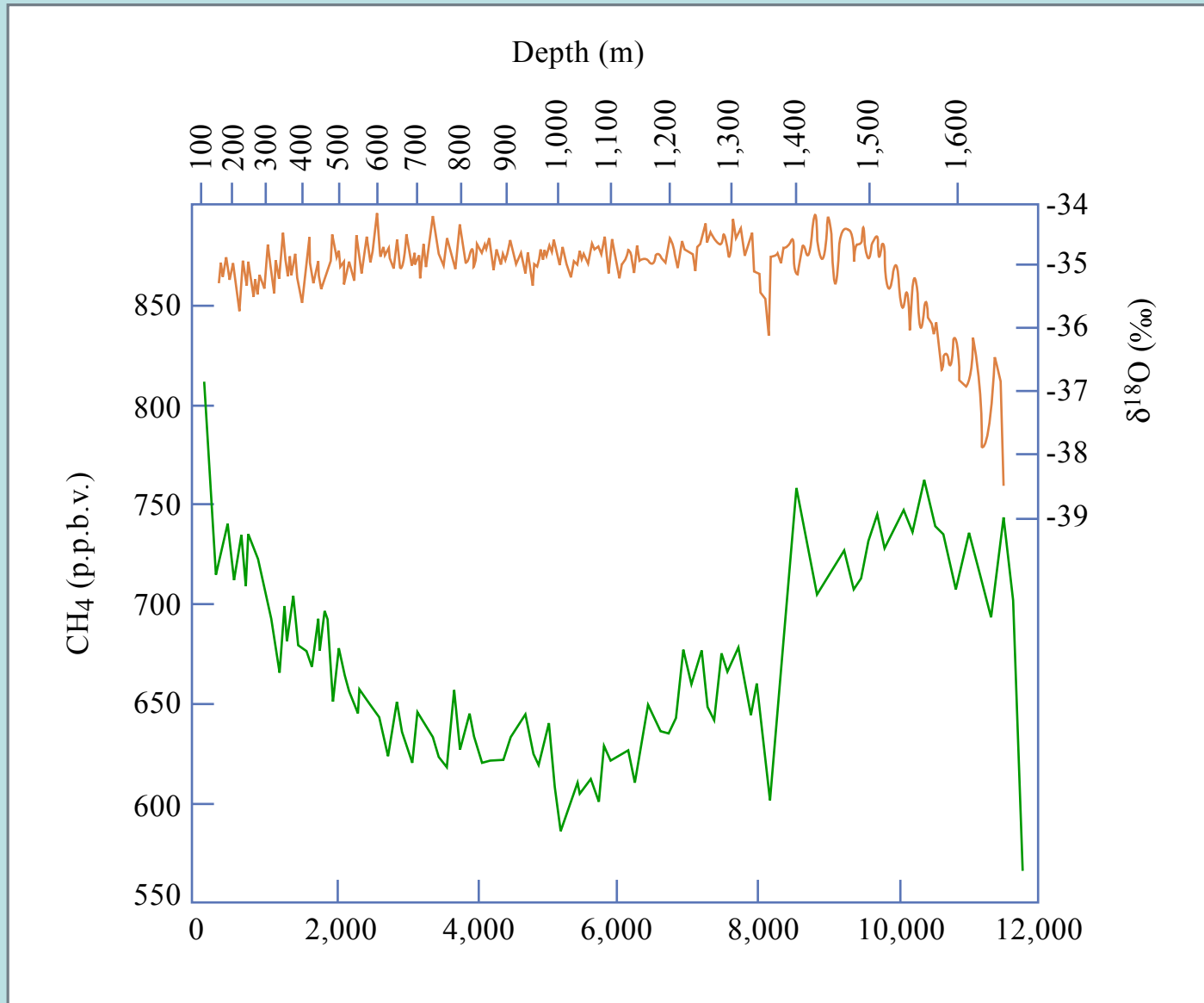


Figure by MIT OCW.

High resolution
records of CH₄ for
the past 110,000
years

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Citation: Figure 1. Brook, et al. *Science* 273 (August 23, 1996): 1089.

used for ice core
correlation

Inter-hemispheric CH₄
gradient existed for most of
the past 10,000 years
(but gradient changed a bit)

Image removed due to copyright restrictions.

Citation: Figure of "Interpolar CH₄ gradient over the holocene."

Chappellaz, J., T. Blunier, Kints S., A. Dällenbach, J. M. Barnola, J. Schwander,
D. Raynaud, and B. Stauffer. "Changes in the Atmospheric CH₄ Gradient between
Greenland and Antarctic During the Holocene." *J Geophys Res* 102 (1997): 15987-15997.

CH₄ hydrates

- Methane forms a solid cage-like compound (clathrate) with water under certain high-pressure/low-temperature regimes. It is estimated that a very large reservoir exists in this form globally - possibly larger than all other fossil fuel reserves. A significant advantage to using CH₄ instead of other fossil fuels is that it emits half the carbon per unit energy released. Is CH₄ clathrate recoverable economically, or is it similar to fusion power (always 50 years away)? One source estimated that the first commercial CH₄ hydrate gas production may begin in 10-15 years (Science 303:944-947, 2004).
- Below the zone of methane hydrate stability (due to geothermal gradient), methane reverts to a gas phase and forms bubbles. The transition from solid methane hydrate to bubbles results in a strong acoustic impedance transition and a “bottom simulating reflector” (BSR).

Methane hydrate
stability field:
cold T, high P

Image removed due to copyright restrictions.

Citation: Figure 1. Miles, P. R. "Potential Distribution of Methane Hydrate Beneath the European Continental Margins." *Geophys Res Lett* 22 (1995): 3179-3182.

Image removed due to copyright restrictions.

Citation: Figure 4. Kvenvolden, K. A. *Rev Geophys* 31 (1993): 173-187.

Significant quantities of methane hydrates exist in Northern tundra/permafrost, so climate warming may result in enhanced methane releases from their decomposition.

Catastrophic releases of methane hydrates: climate, earthquake, and tsunami connections?

- There is some evidence that methane hydrates can decompose rapidly due to rising temperature and/or lower pressure due to falling sea level or glacial melting.
- Some modeling (C. Ruppel) suggests that it is difficult to decompose the methane hydrate quickly (because the reaction is endothermic and counteracts the diffusion of heat. So climate warming by itself may not be sufficient.
- There is evidence for a link between massive submarine landslides and methane hydrates. Could methane hydrate decomposition set off these landslides (and tsunamis)?
- A major submarine landslide in the Norwegian Sea 8200 years ago (“Storegga Slide”, which caused drastic tsunamis) occurred at the same time as a significant climate cooling seen in the Greenland ice cores (chicken, egg, or coincidence?). Earthquake triggering of slope failure (involving hydrate amplification) also has been suggested.
- It has been suggested that methane hydrate releases may have produced abrupt climate change during the past 60,000 years (J. Kennett).

Seafloor “pockmarks” in the Arctic Ocean have been attributed to catastrophic methane hydrate decomposition

Image removed due to copyright restrictions.

Citation: Figure 4. Henriot, J. P., and J. Mienert. *Gas Hydrates, Relevance to World Margin Stability and Climatic Change*. The Geological Society, London, 1998.

Some people have suggested that ships might have been lost at sea during hydrate releases (methane bubbles having reduced the density of water and hence the buoyancy of the ship).

Storegga
Slide
~8200 yrBP

Sent a 10 m
high tsunami
into the
northern coast
of Europe

? Triggered by
earthquake
and/or
catastrophic
CH₄ hydrate
decomposition?

Paleocene/Eocene Thermal Maximum (PETM)

Image removed due to copyright restrictions.

Citation: Figure 12. *Nature* 353: 225-229.

Clay layer occurring
in deep sea sediments
2.7-4.8 indicates
acidification of ocean
by the CO₂ released
during this event
(Zachos et al., 2005,
Science 308:1611)

Runaway methane?

Image removed due to copyright restrictions.

Citation: Figure 1. Prather, M. J. "Time Scales in Atmospheric Chemistry: Theory, GWPs for CH₄ and C, and Runaway Growth." *Geophys Res Lett* 23 (1996): 2597-2600.