Geochemical Cycles

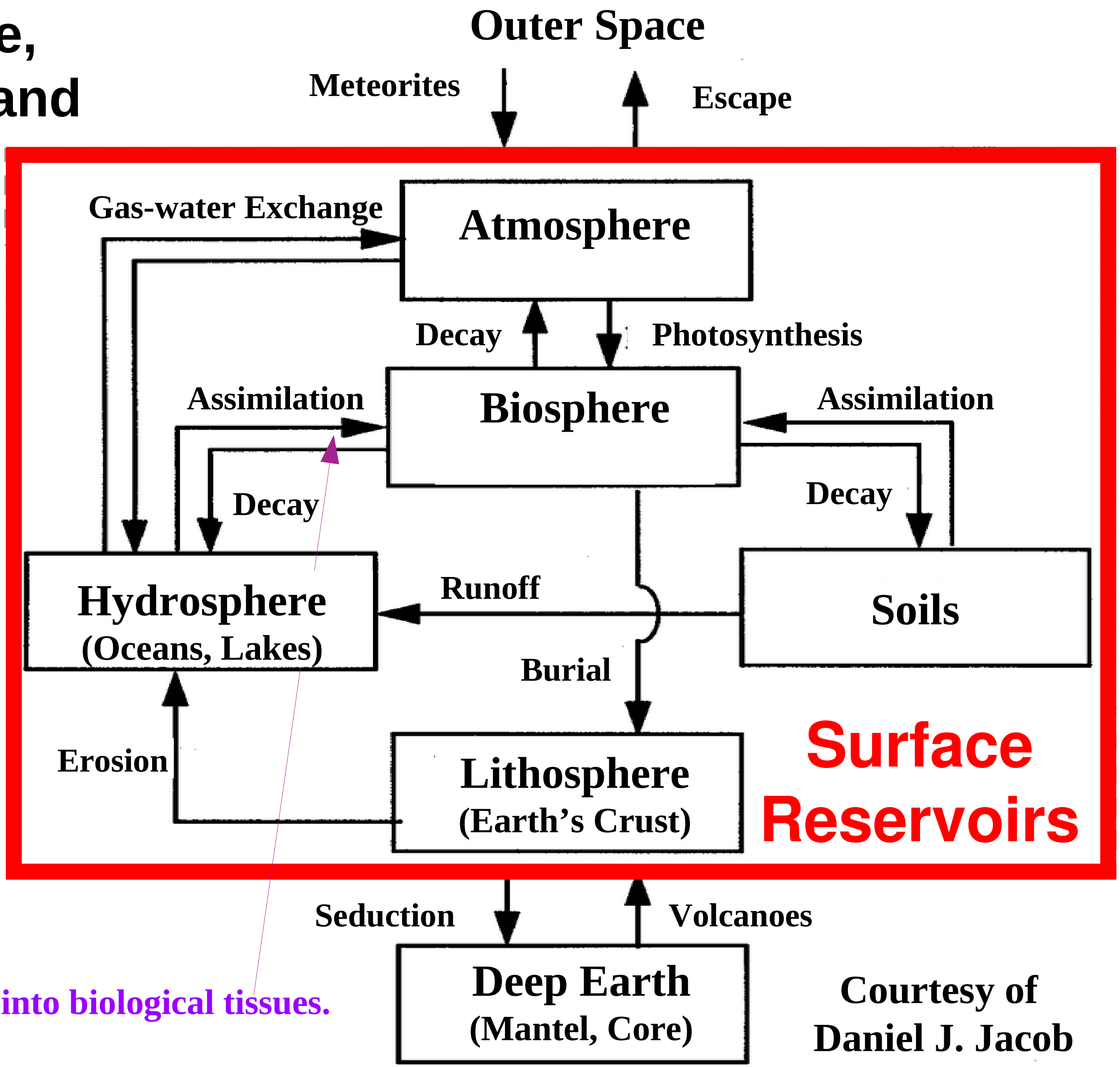
The Earth is an assemblage of atoms of the 92 natural elements.

- **Most Abundant Elements: oxygen (in solid earth!), iron (core), silicon (mantle), hydrogen (oceans), nitrogen, carbon, sulfur…**
- **The elemental composition of the Earth has remained essentially unchanged over its 4.5 Gyr (billion year) history.**
  - **Extraterrestrial inputs (e.g., from meteorites, cometary material) have been relatively unimportant.**
  - **Escape to space has been restricted by gravity.**
- ***Biogeochemical Cycling* of elements between the different reservoirs of the Earth system determines the composition of the Earth's atmosphere and oceans, and the evolution of life.**

Example of Major Processes

Physical exchange, redox chemistry, and biochemistry are involved.

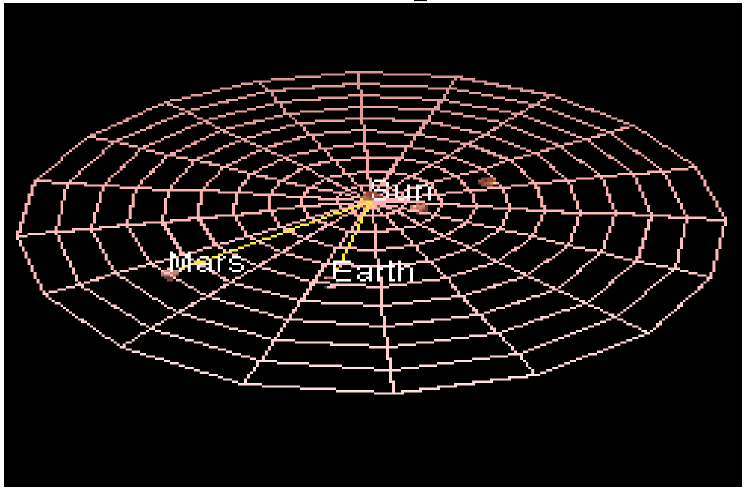
Redox reactions, or oxidation-reduction reactions, are a family of reactions that are concerned with the transfer of electrons between species. Like acid-base reactions, redox reactions are a matched set. Oxidation refers to the loss of electrons, while reduction refers to the gain of electrons. Each reaction by itself is called a "half-reaction", simply because we need two half-reactions to form a whole reaction.



Assimilation – Incorporation into biological tissues.

Courtesy of Daniel J. Jacob

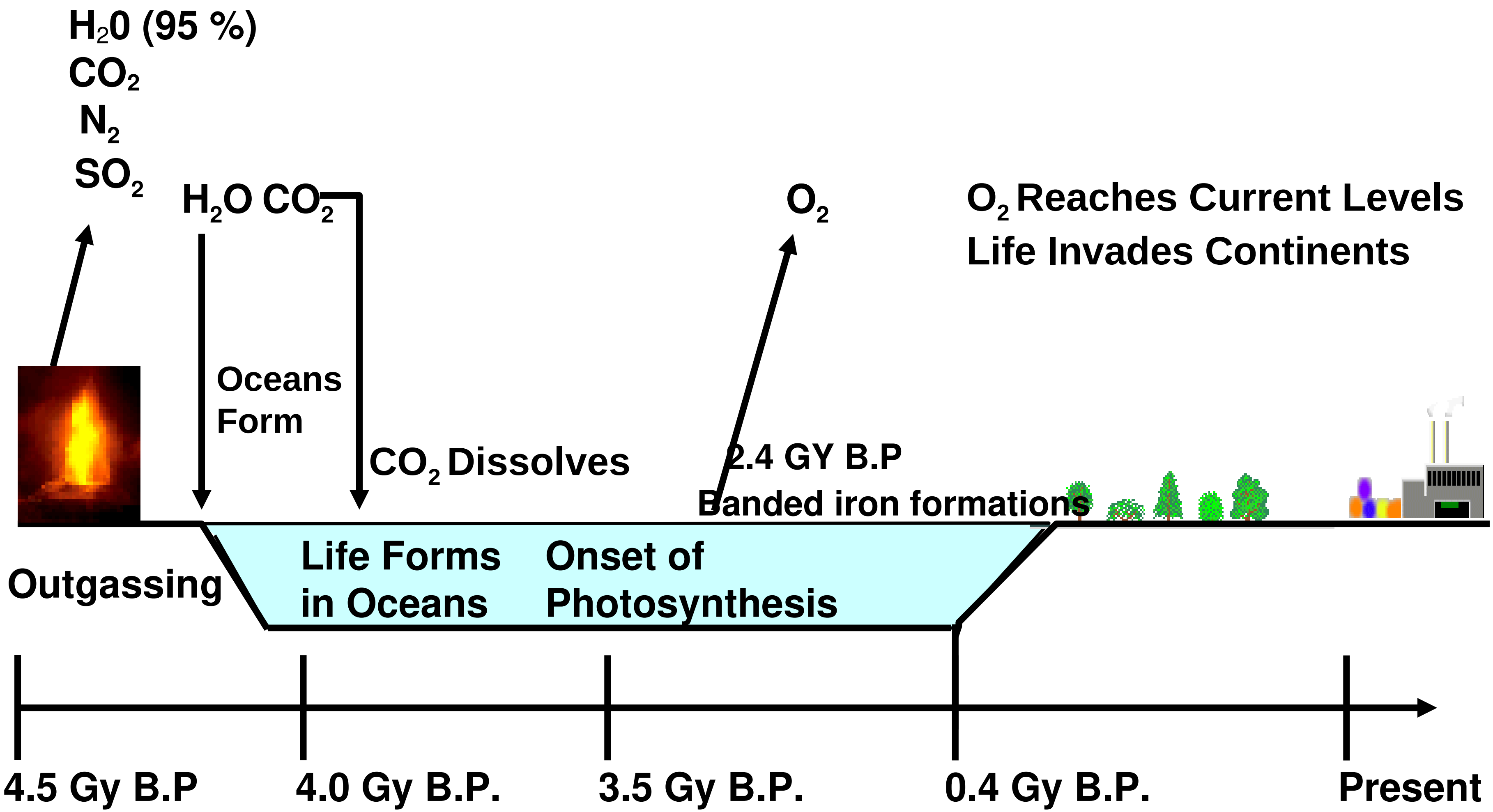
Comparison of Atmospheres



	Venus	Earth	Mars
Radius (km)	6100	6400	3400
Surface Pressure (atm)	91	1	0.007
CO_2 (mol/mol)	0.96	3×10^{-4}	0.95
N_2 (mol/mol)	3.4×10^{-2}	0.78	2.7×10^{-2}
O_2 (mol/mol)	6.9×10^{-5}	0.21	1.3×10^{-3}
H_2O (mol/mol)	3×10^{-3}	1×10^{-2}	3×10^{-4}

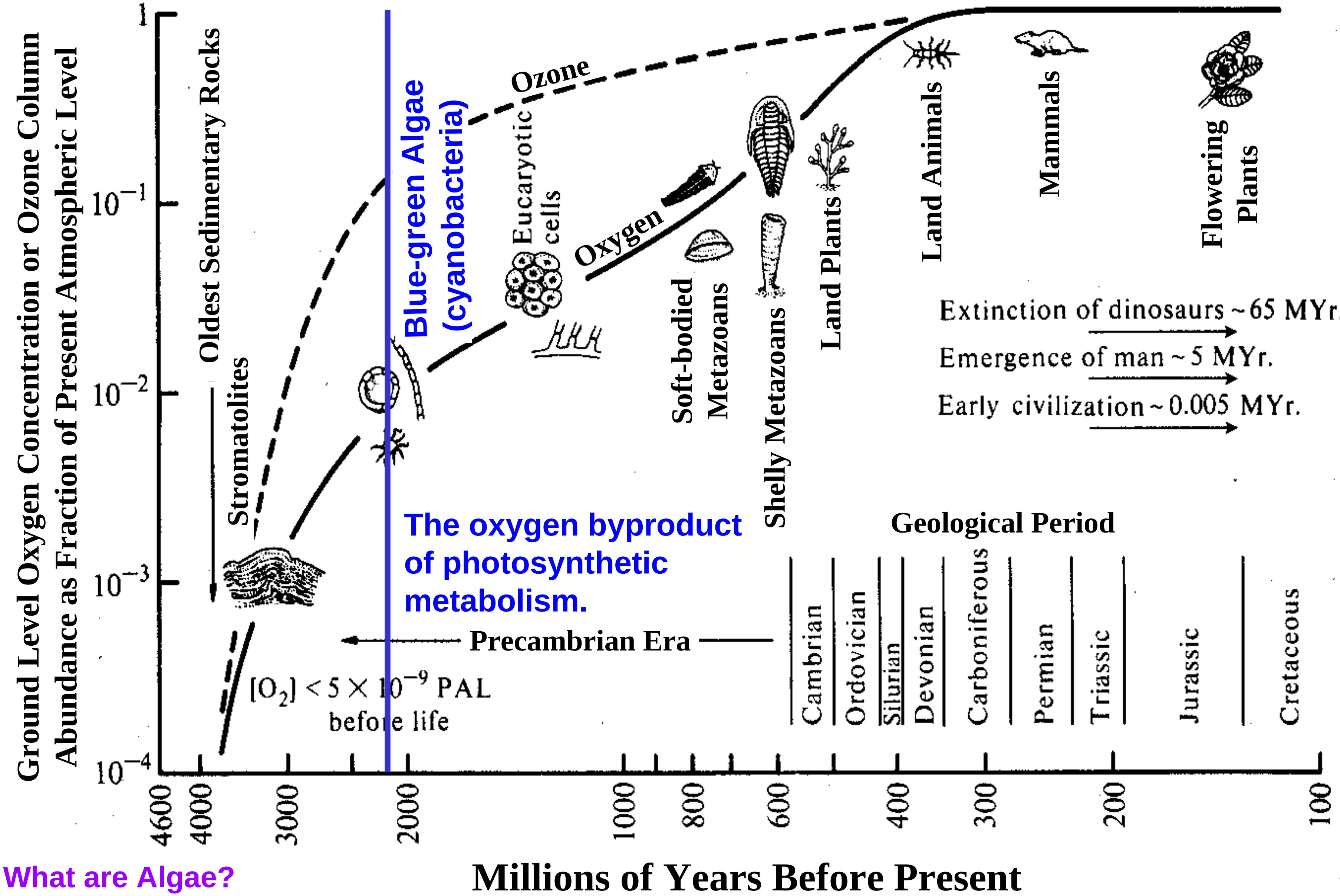
History of the Earth' Atmosphere



Note: B.P. is Before Present

Courtesy of Daniel J. Jacob

Atmospheric Evolution of O_2 and O_3



What are Algae?

Has O_2 declined recently?

Why the slow increase in O_2?

Original figure courtesy of Daniel J. Jacob, text added.

Earth's Atmospheric Gas Composition

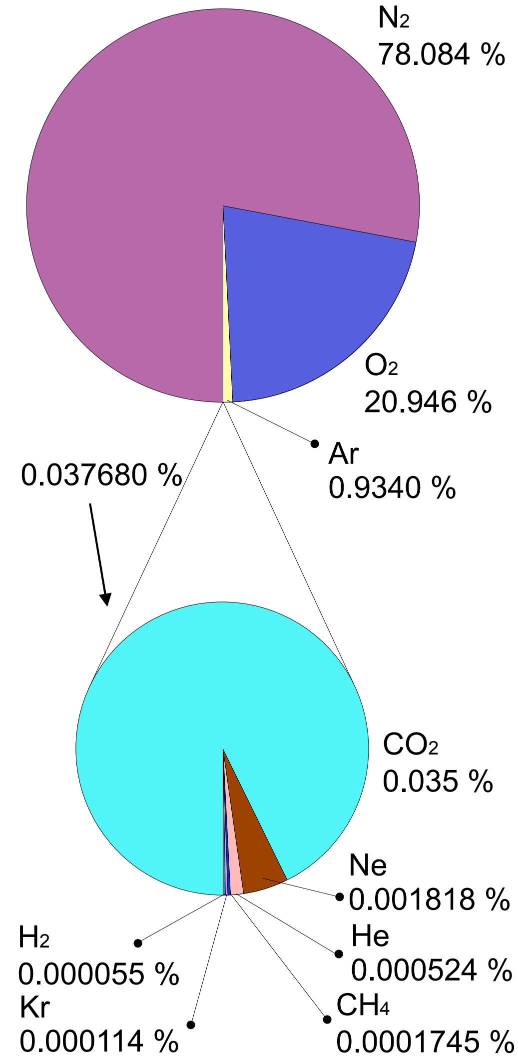
Mixing Ratio or Mole Fraction C_X [mol mol^{-1}]

$$C_X = \frac{\text{\# moles of X}}{\text{mole of air}}$$

Remains constant when air density changes; therefore, a robust measure of atmospheric composition

GAS	MIXING RATIO (dry air) [mol mol^{-1}]
Nitrogen (N_2)	0.78
Oxygen (O_2)	0.21
Argon (Ar)	0.0093
Carbon dioxide (CO_2)	380×10^{-6}
Neon (Ne)	18×10^{-6}
Ozone (O_3)	$(0.01\text{-}10) \times 10^{-6}$
Helium (He)	5.2×10^{-6}
Methane (CH_4)	1.7×10^{-6}
Krypton (Kr)	1.1×10^{-6}

Trace Gases (carbon dioxide through methane)



Air also contains variable H_2O vapor (10^{-6}-10^{-2} mol mol^{-1}) or locally 0.001%-3%.

Trace gas concentration units:

1 ppmv = 1 μmol mol^{-1} = 1×10^{-6} mol mol^{-1}

1 ppbv = 1 nmol mol^{-1} = 1×10^{-9} mol mol^{-1}

1 pptv = 1 pmol mol^{-1} = 1×10^{-12} mol mol^{-1}

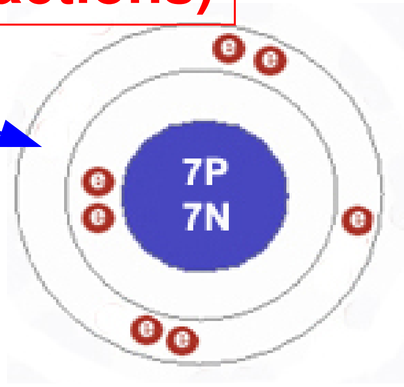
Nitrogen Oxidation States

Increasing Oxidation Number (Oxidation Reactions) →

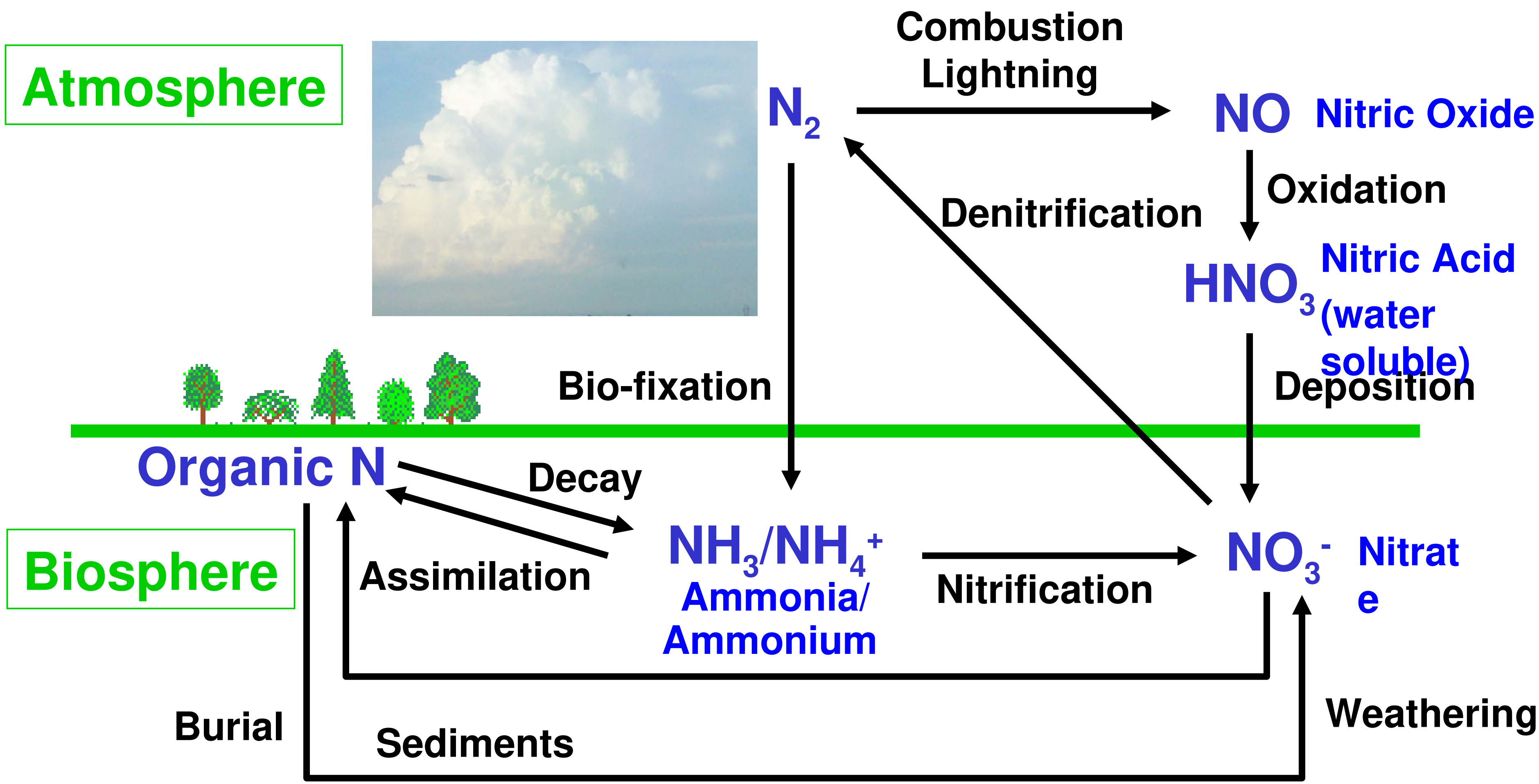
-3	0	+1	+2	+3	+4	+5
NH_3 **Ammonia** NH_4^+ **Ammonium** $R_1N(R_2)R_3$ **Organic N**	N_2	N_2O **Nitrous Oxide**	NO **Nitric Oxide** *Radical*	$HONO$ **Nitrous Acid** NO_2^- **Nitrite**	NO_2 **Nitrogen Dioxide** *Radical*	HNO_3 **Nitric Acid** NO_3^- **Nitrate**

← **Decreasing Oxidation Number (Reduction Reactions)**

N has 5 electrons in valence shell and 9 oxidation states from –3 to +5.



The Nitrogen Cycle



What are the biologically available forms Nitrogen?

To make NH_3 from Atmospheric Nitrogen, what do you need?

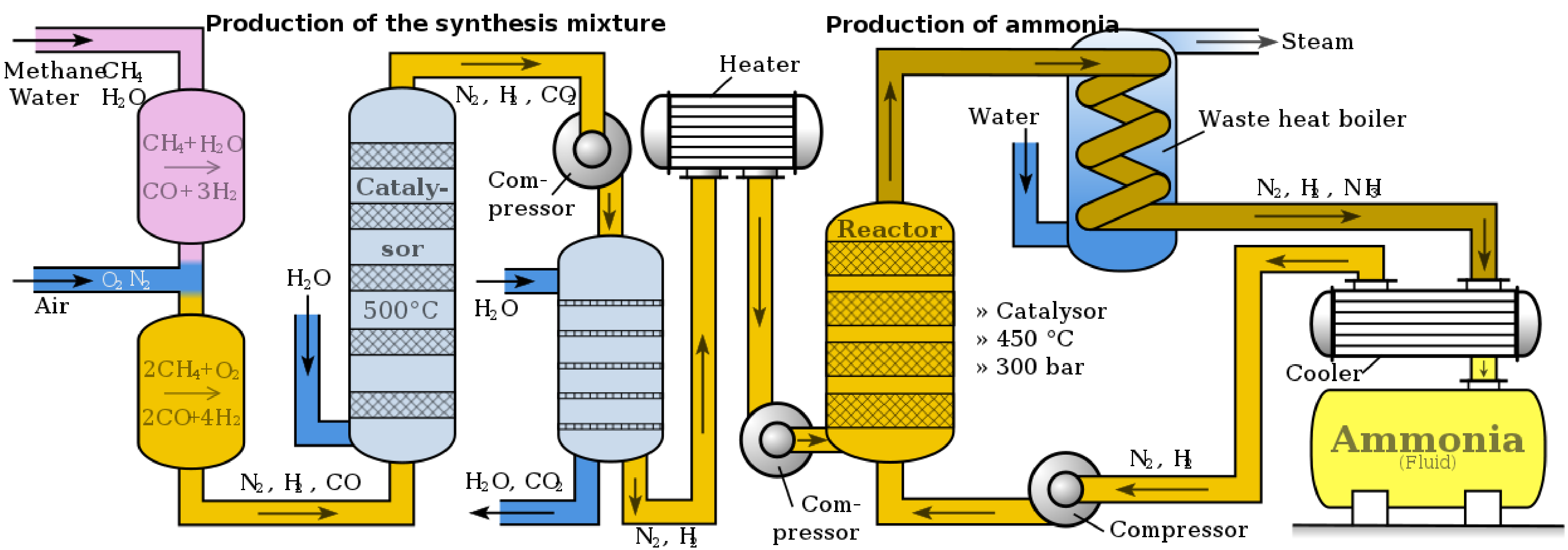
Courtesy of Daniel J. Jacob

Ammonia Synthesis – Haber Process

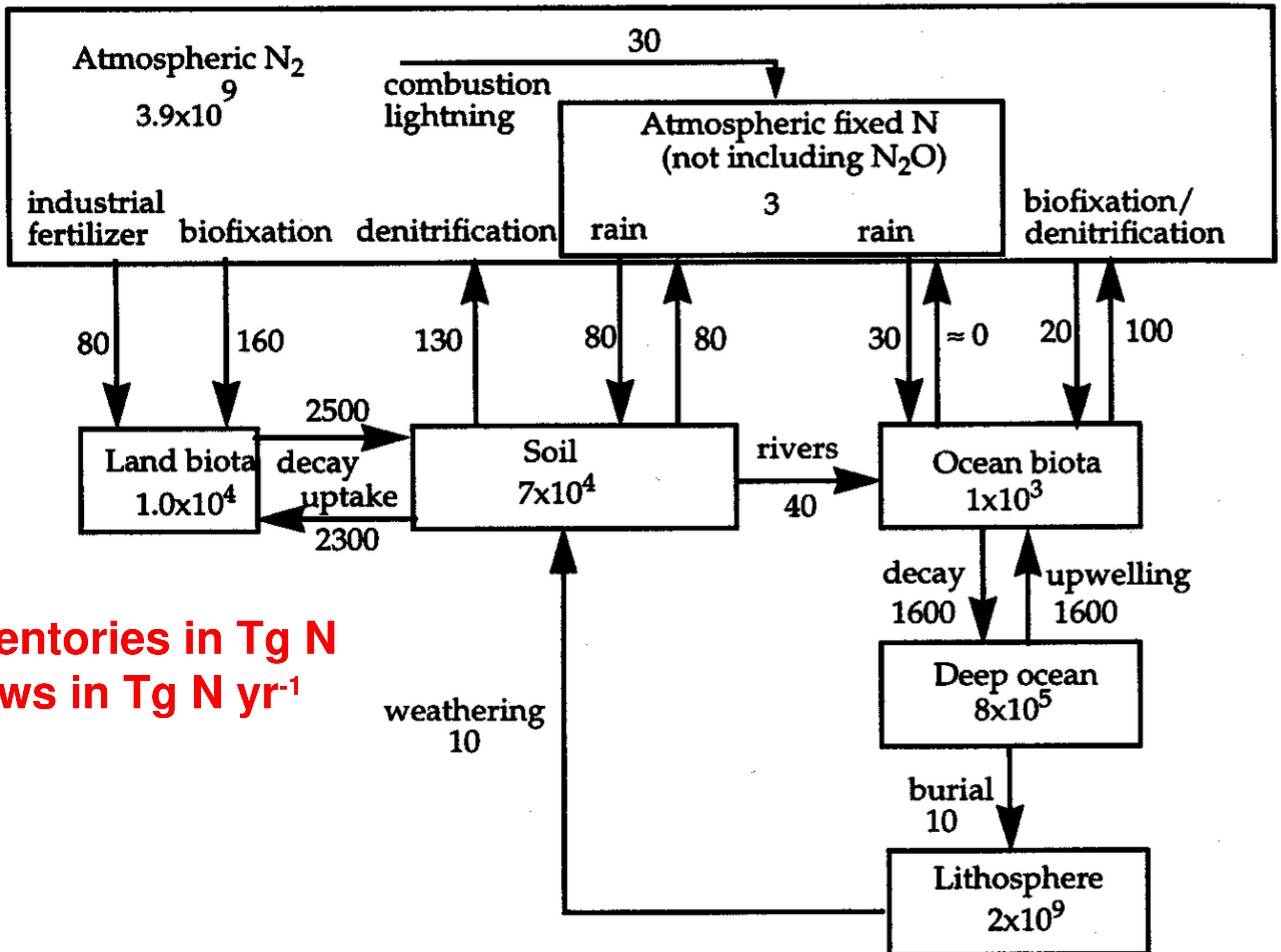
The synthesis of ammonia using an iron catalyst promoted with K_2O, CaO, and Al_2O_3:

$$N_2\ (g) + 3\ H_2\ (g) \rightleftharpoons 2\ NH_3\ (g) \quad (\Delta H = -92.22\ kJ \cdot mol^{-1})$$

Reaction is done at 15–25 Mpa (150–250 bar) and between 300 and 550 °C



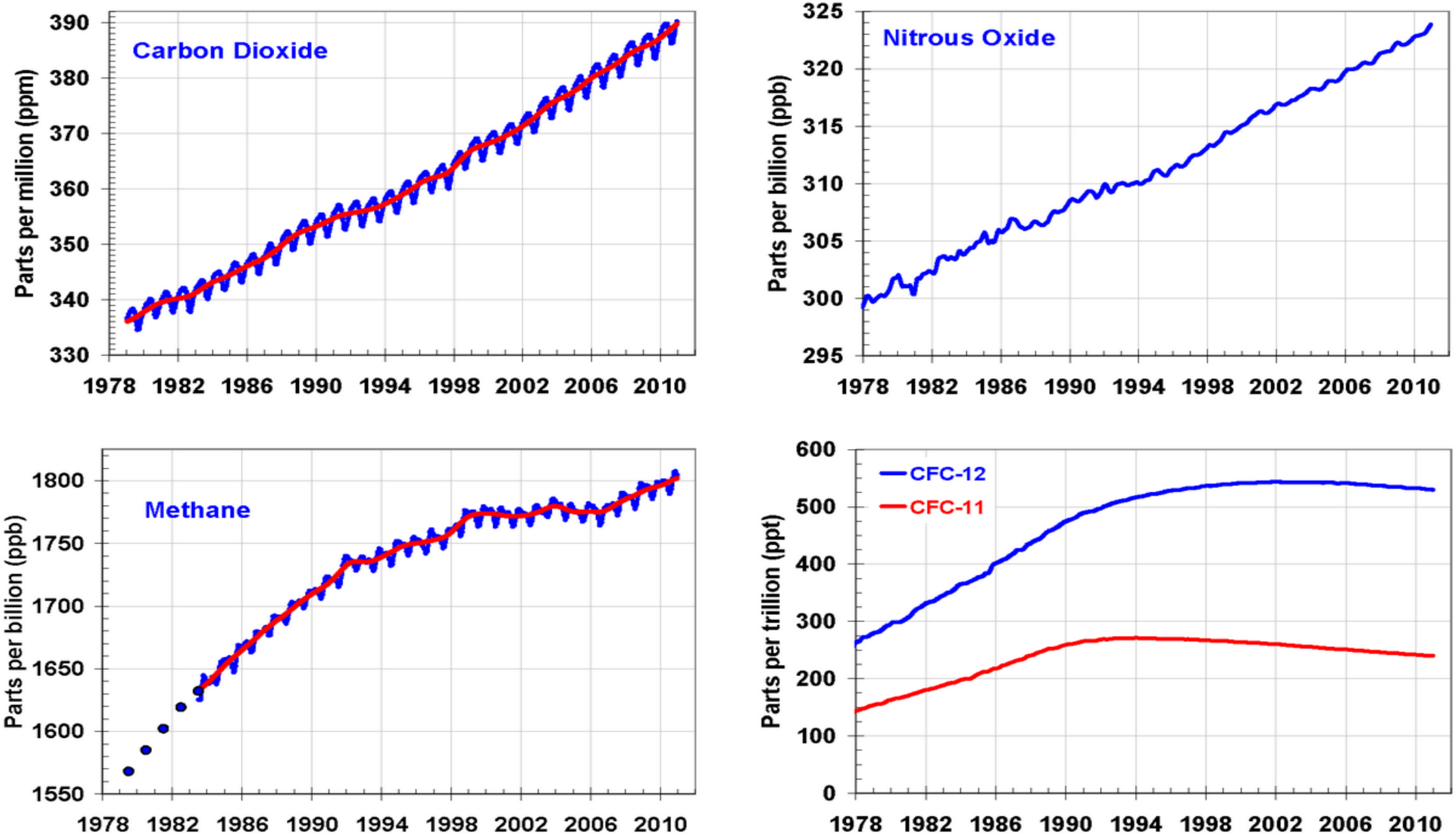
Box Model of the Nitrogen Cycle



Inventories in Tg N
Flows in Tg N yr^{-1}

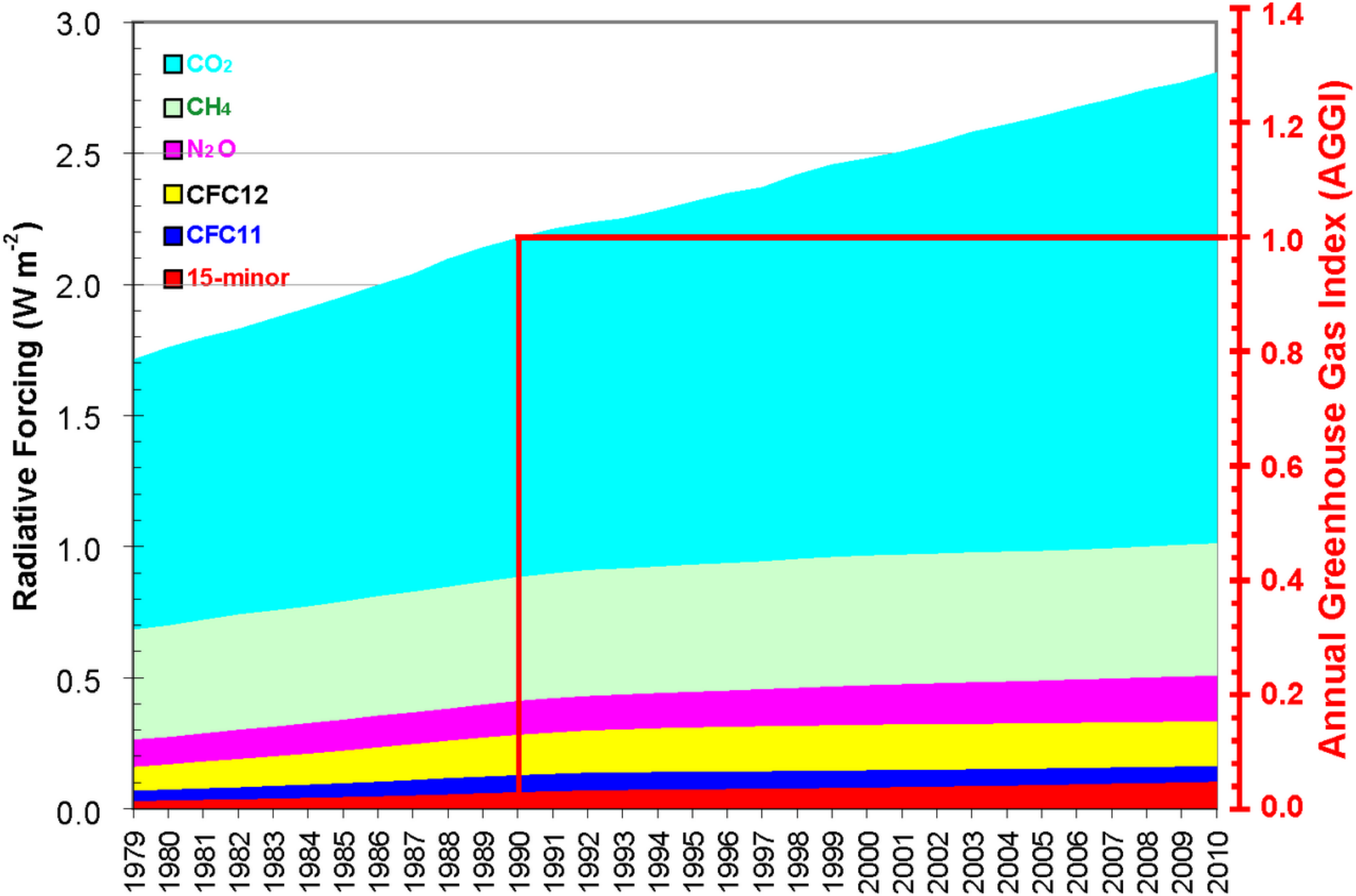
Courtesy of Daniel J. Jacob

NOAA Greenhouse Gas Measurements



Global average abundances of the major, well-mixed, long-lived greenhouse gases - carbon dioxide, methane, nitrous oxide, CFC-12 and CFC-11 - from the NOAA global air sampling network are plotted since the beginning of 1979. These gases account for about 96% of the direct radiative forcing by long-lived greenhouse gases since 1750. The remaining 4% is contributed by an assortment of 15 minor halogenated gases (see text). Methane data before 1983 are annual averages from Etheridge et al. (1998), adjusted to the NOAA calibration scale [Dlugokencky et al., 2005].

NOAA Annual Greenhouse Gas Index

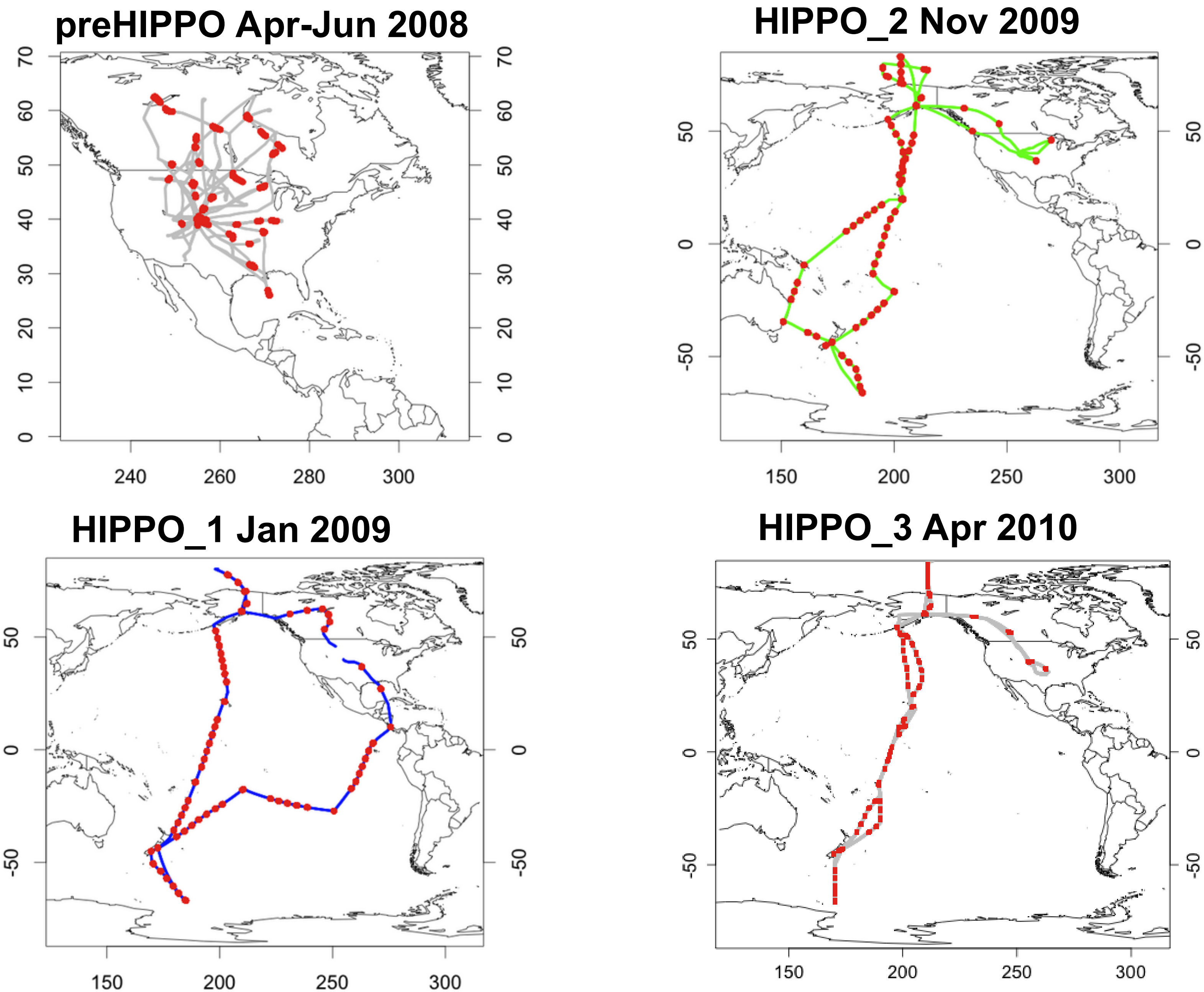


Radiative forcing, relative to 1750, of all the long-lived greenhouse gases. The NOAA Annual Greenhouse Gas Index (AGGI), which is indexed to 1 for the year 1990, is shown on the right axis.

HIPPO boat: NCAR Gulfstream V "HIAPER"

GV launch in the rain, Anchorage, January, 2009 (HIPPO-1)

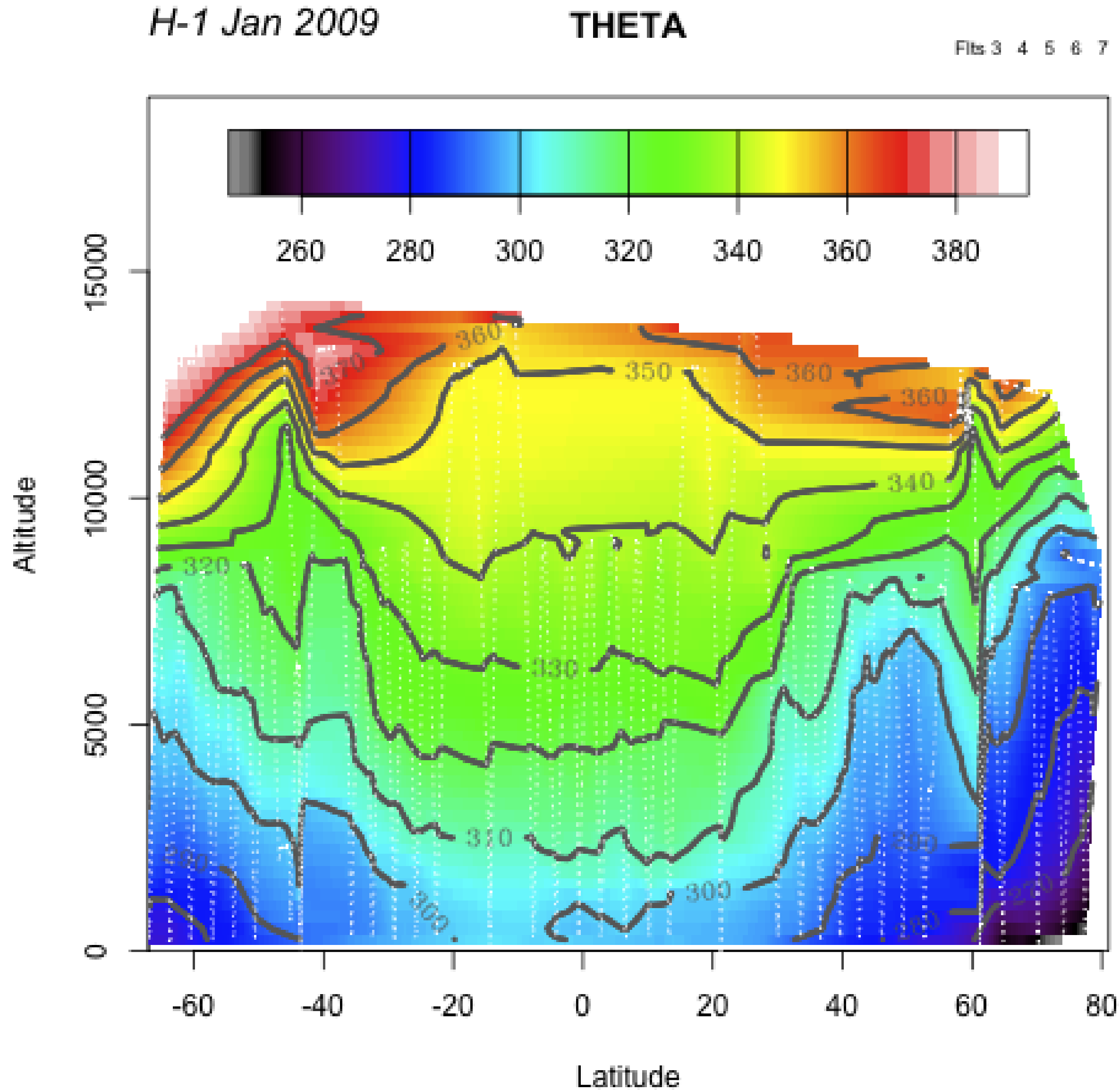
Courtesy of Daniel J. Jacob



Courtesy of Daniel J. Jacob

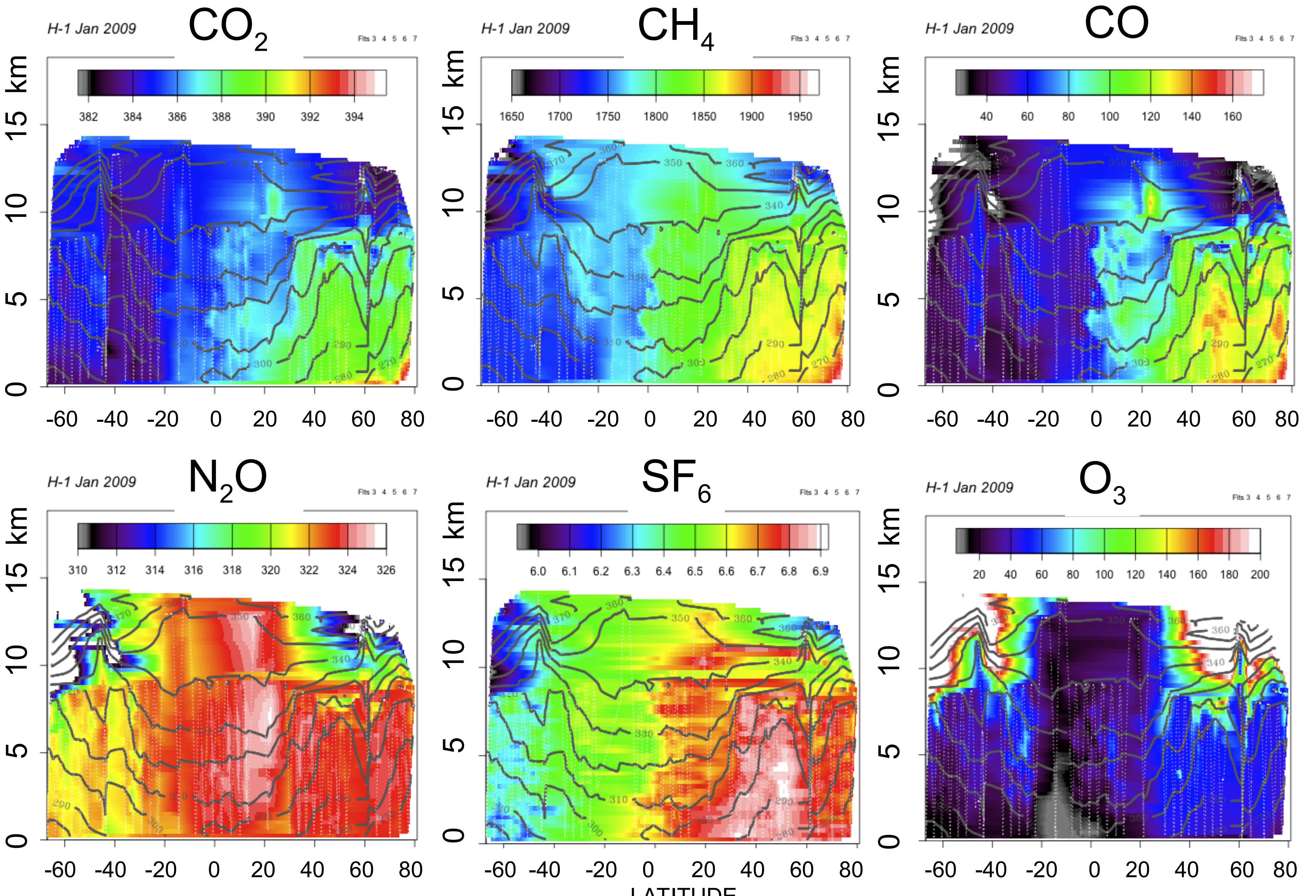
HIPPO-1 Atmospheric Structure (Pot'l T K):

January, 2009, Mid-Pacific (Dateline) Cross section



Courtesy of Daniel J. Jacob

HIPPO Sections, January 2009



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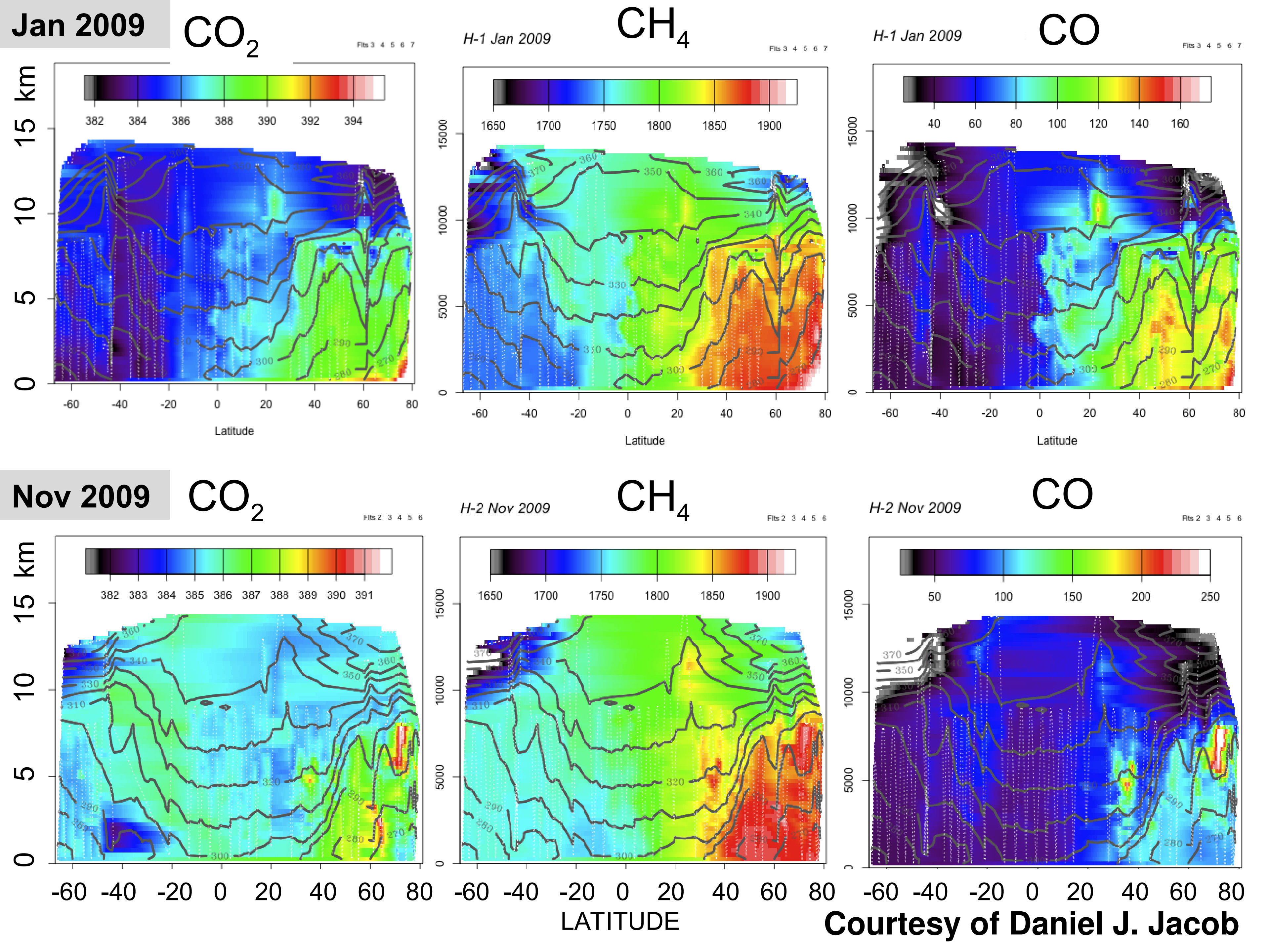
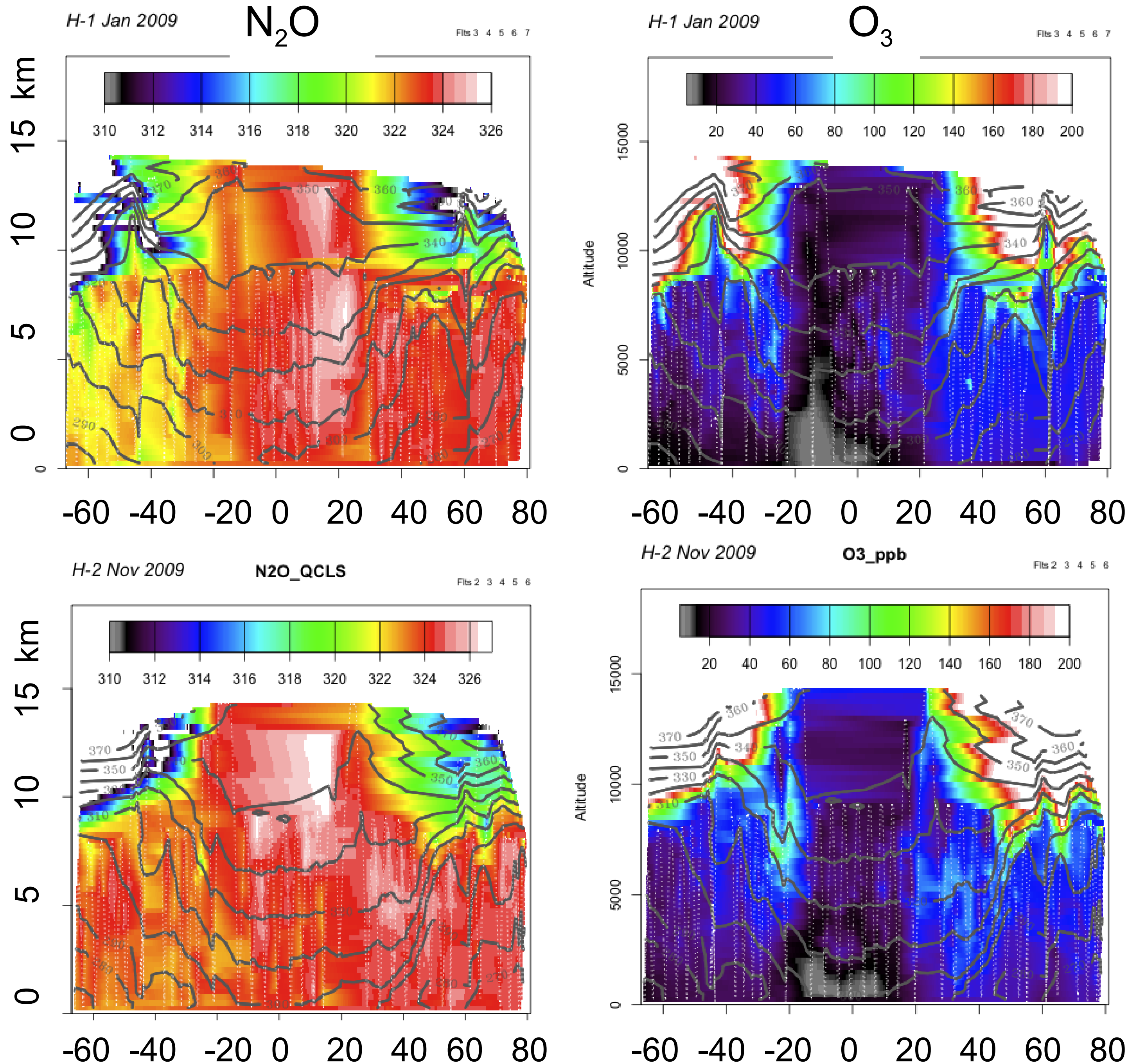

Jan 2009
CO2
H-1 Jan 2009
CH4
H-1 Jan 2009
CO
km
Latitude
Nov 2009
CO2
H-2 Nov 2009
CH4
H-2 Nov 2009
CO
LATITUDE
Courtesy of Daniel J. Jacob

January 2009

November 2009



LATITUDE Courtesy of Daniel J. Jacob