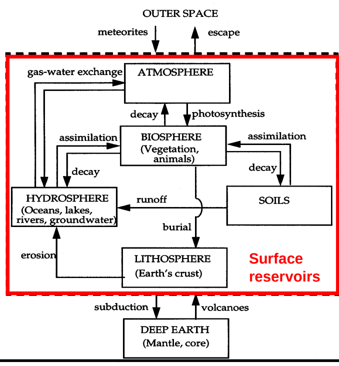
CHAPTER 6: GEOCHEMICAL CYCLES

THE EARTH: ASSEMBLAGE OF ATOMS OF THE 92 NATURAL ELEMENTS

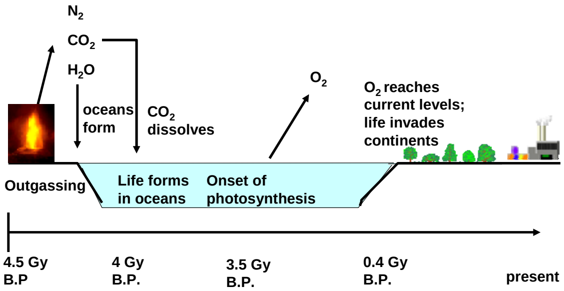
- **Most abundant elements:** oxygen (in solid earth!), iron (core), silicon (mantle), hydrogen (oceans), nitrogen, carbon, sulfur…
- **The elemental composition of the Earth has remained essentially unchanged over its 4.5 Gyr history**
  - Extraterrestrial inputs (e.g., from meteorites, cometary material)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

BIOGEOCHEMICAL CYCLING OF ELEMENTS: examples of major processes

Physical exchange, redox chemistry, biochemistry are involved



HISTORY OF EARTH'S ATMOSPHERE



QUESTIONS

1. How do elements in the lithosphere get transferred to the atmosphere?

2. Imagine an early Earth with a weak Sun and frozen ocean ("snowball Earth"). How would volcanic activity eventually warm the Earth and cause melting of the ocean?

Atmospheric Composition (average)

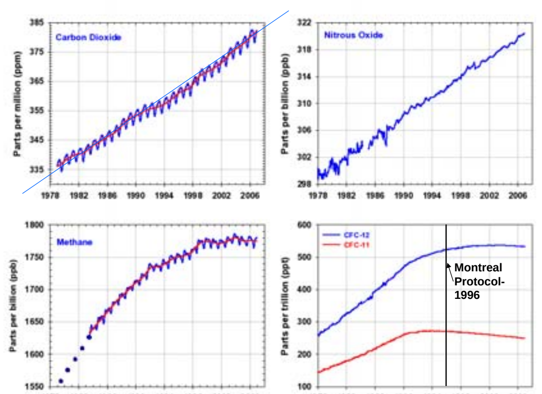
1 ppm= $1x10^{-6}$

red = increased by human activity

Gas	*Mole fraction*
Nitrogen (N_2)	0.78
Oxygen (O_2)	0.21
Water (H_2O)	0.04 to < $5x10^{-3}$; $4x10^{-6}$ -strat
Argon (Ar)	0.0093
Carbon Dioxide (CO_2)	$370x10^{-6}$ (date: 2000)
Neon (Ne)	$18.2x10^{-6}$
Ozone (O_3) ¶	$0.02x10^{-6}$ to $10x10^{-6}$
Helium (He)	$5.2x10^{-6}$
Methane (CH_4)	$1.7x10^{-6}$
Krypton (Kr)	$1.1x10^{-6}$
Hydrogen (H_2)	*$0.55x10^{-6}$*
Nitrous Oxide (N_2O)	$0.32x10^{-6}$
Carbon Monoxide (CO)	$0.03x10^{-6}$ to $0.3x10^{-6}$
Chlorofluorocarbons	$3.0x10^{-9}$
Carbonyl Sulfide (COS)	$0.1x10^{-9}$

¶ Ozone has increased in the troposphere, but decreased in the stratosphere.

NOAA Greenhouse Gas records



OXIDATION STATES OF NITROGEN

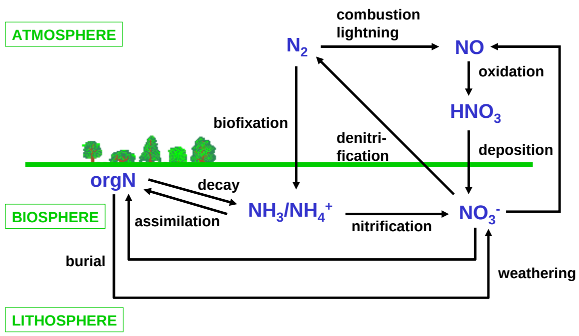
N has 5 electrons in valence shell ⇨ 9 oxidation states from –3 to +5

Increasing oxidation number (oxidation reactions) →

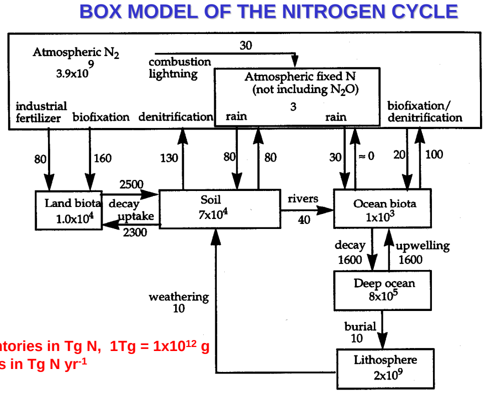
-3	0	+1	+2	+3	+4	+5
NH_3 Ammonia NH_4^+ Ammonium $R_1N(R_2)R_3$ Organic N	N_2	N_2O Nitrous oxide	NO Nitric oxide	HONO Nitrous acid NO_2^- Nitrite	NO_2 Nitrogen dioxide	HNO_3 Nitric acid NO_3^- Nitrate

← Decreasing oxidation number (reduction reactions)

THE NITROGEN CYCLE: MAJOR PROCESSES



BOX MODEL OF THE NITROGEN CYCLE



Inventories in Tg N, 1Tg = 1×10^{12} g
Flows in Tg N yr^{-1}

QUESTION

1. What if denitrification shut off while N_2 fixation still operated? How long would it take for the atmosphere to be depleted of N_2?

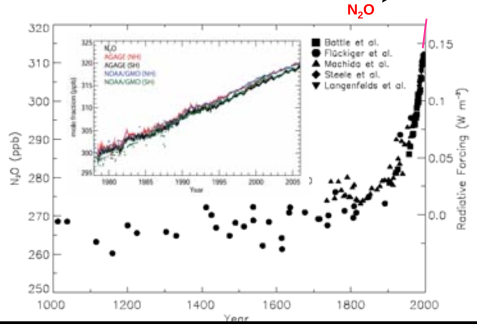
N_2O: LOW-YIELD PRODUCT OF BACTERIAL NITRIFICATION AND DENITRIFICATION

Important as
- source of NO_x radicals in stratosphere
- greenhouse gas

$NH_4^+ + 3/2O_2 \Rightarrow NO_2^- + H_2O + 2\,H^+$

$NO_3^- + \text{Org-C} \Rightarrow N_2 + \ldots$

N_2O



IPCC [2007]

PRESENT-DAY GLOBAL BUDGET OF ATMOSPHERIC N_2O

SOURCES (Tg N yr^{-1})	18 (7 – 37)
Natural	10 (5 – 16)
Ocean	3 (1 - 5)
Tropical soils	4 (3 – 6)
Temperate soils	2 (1 – 4)
Anthropogenic	8 (2 – 21)
Agricultural soils	4 (1 – 15)
Livestock	2 (1 – 3)
Industrial	1 (1 – 2)
SINK (Tg N yr^{-1}) Photolysis and oxidation in stratosphere	12 (9 – 16)
ACCUMULATION (Tg N yr^{-1})	4 (3 – 5)

IPCC [2001]

Although a closed budget can be constructed, uncertainties in sources are large!
(N_2O atm mass = 5.13 10^{18} kg x 3.1 10^{-7} x28/29 = 1535 Tg)

SULFUR CYCLE

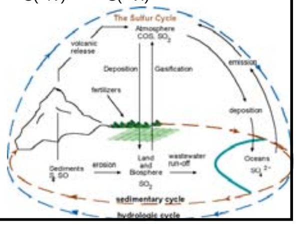
Most sulfur is tied up in sediments and soils. There are large fluxes to the atmosphere, but with **short atmospheric lifetimes**, the atmospheric S burden is small.

SO_2: Anthropogenic (fossil fuel combustion) source comparable to natural sources (soils, sediments, volcanoes)

Sulfur is oxidized in the atmosphere: SO_2 ---- > H_2SO_4
S(+IV) S(+VI)

Sulfate is an important contributor to acidity of precipitation. Sulfuric acid has a low P_{vap} and thus partitions primarily to aerosol/aqueous phase

Strongly perturbed by human activities!



Oxidation states of sulfur

Increasing oxidation number (oxidation reactions)

-2	-1	0	+4	+6
$H_2S(g)$ **Hydrogen sulfide** $CS_2(g)$ **Carbon disulfide** CH_3SCH_3 **Dimethyl sulfide (DMS)** OCS **Carbon sulfide**	$CH_3SSCH_3(g)$ **Dimethyl disulfide**	$CH_3SOCH_3(g)$ **Dimethyl sulfoxide**	SO_2 (g) **Sulfur dioxide** HSO_3^-(aq) **Bisulfite** SO_3^{2-}(aq) **Sulfite** CH_3SO_3H (aq) **Methane sulfonic acid (MSA)**	H_2SO_4 (aq) **Sulfuric acid** HSO_4^- (aq) **Bisulfate** SO_4^{2-} (aq) **Sulfate**

Decreasing oxidation number (reduction reactions)

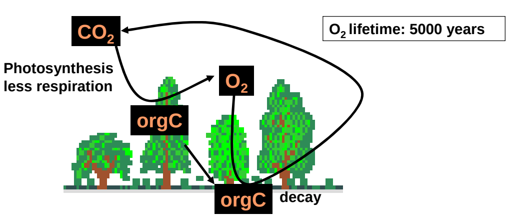
FAST OXYGEN CYCLE: ATMOSPHERE-BIOSPHERE

- **Source of O_2: photosynthesis**

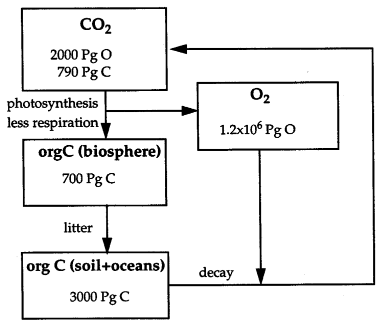
  $$nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2$$

- **Sink: respiration/decay**

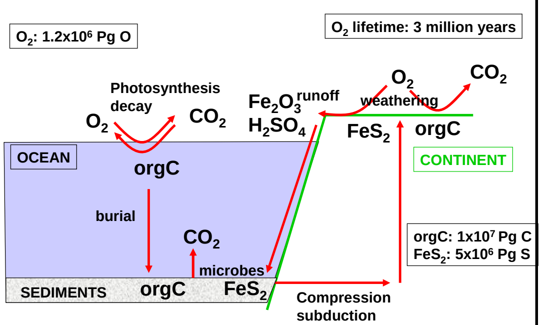
  $$(CH_2O)_n + nO_2 \rightarrow nCO_2 + nH_2O$$



…however, abundance of organic carbon in biosphere/soil/ocean reservoirs is too small to control atmospheric O_2 levels



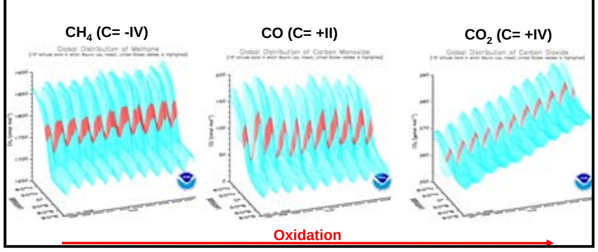
SLOW OXYGEN CYCLE: ATMOSPHERE-LITHOSPHERE



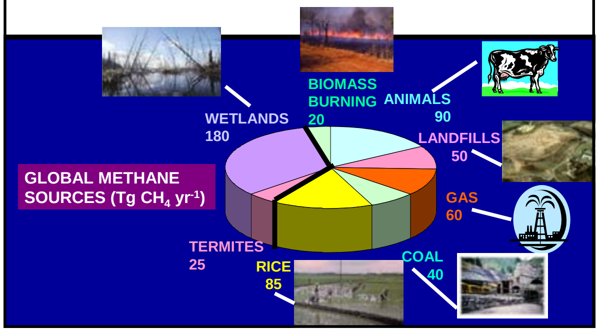
ATMOSPHERIC CARBON

Unreactive Carbon: CO_2: GHG (more to follow…) (τ_{ATM}~20 yrs)

Reactive Carbon:
- CH_4: GHG, important in oxidant chemistry (τ_{ATM}~9 yrs)
- CO: important in oxidant chemistry (later…) (τ_{ATM}~2 mos)
- NMHCs: source of CO, oxidant chemistry (τ_{ATM}~sec-mos)
- Black Carbon: radiatively important (τ_{ATM}~days)



SOURCES OF ATMOSPHERIC METHANE



SINKS OF ATMOSPHERIC METHANE

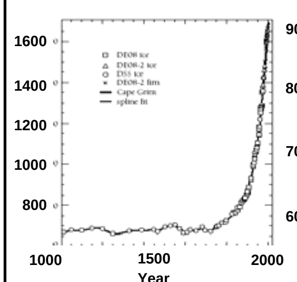
I. Transport to the Stratosphere
Only a few percent, rapidly destroyed → BUT the most important source of water vapor in the dry stratosphere

II. Oxidation
$CH_4 + OH \rightarrow CH_3O_2 \xrightarrow{O_2} CO$ + other products

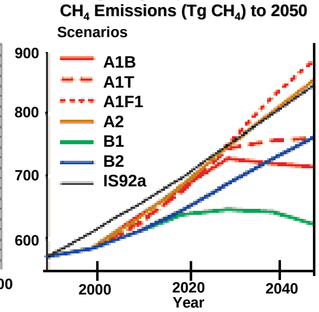
Lifetime ~ 9 years

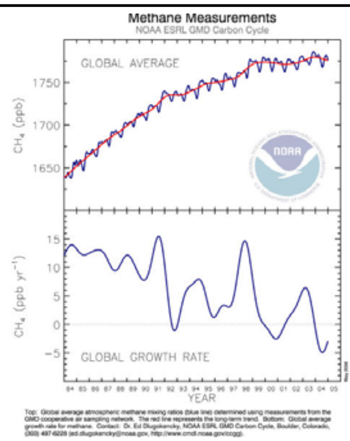
ATMOSPHERIC CH_4: PAST TRENDS, FUTURE PREDICTIONS

Variations of CH_4 Concentration (ppbv) Over the Past 1000 years [*Etheridge et al.*, 1998]

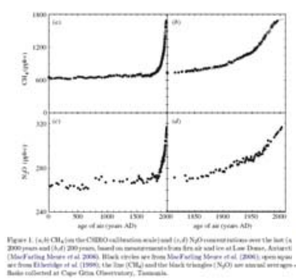


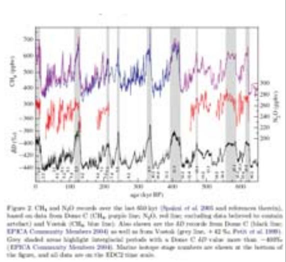
IPCC [2001] Projections of Future CH_4 Emissions (Tg CH_4) to 2050





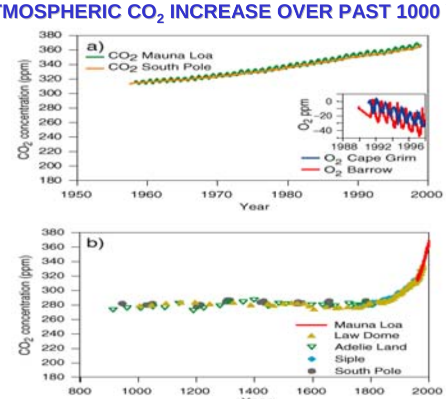
CH_4 and N_2O from the EPICA (Antarctica) ice core





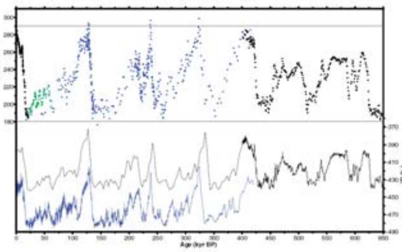
Wolff and Spahini, 2007

ATMOSPHERIC CO_2 INCREASE OVER PAST 1000 YEARS



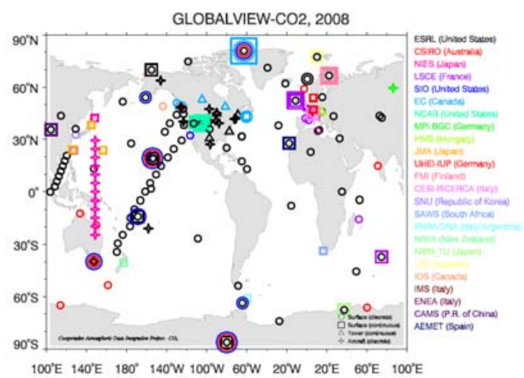
CO_2 from the EPICA (Antarctica) ice core

Fig. 4. A composite CO_2 record over six and a half ice age cycles, back to 650,000 years B.P. The record results from the combination of CO_2 data from three Antarctic ice cores: Dome C (black), 0 to 22 kyr B.P. (9, 11) and 390 to 650 kyr B.P. [this work including data from 31 depth intervals over termination V of (1)], Vostok (blue), 0 to 420 kyr B.P. (5, 7), and Taylor Dome (light green), 20 to 62 yr B.P. (8). Black line indicates δD from Dome C, 0 to 400 kyr B.P. (1) and 400 to 650 kyr B.P. (18). Blue line indicates δD from Vostok, 0 to 420 kyr B.P. (7).



Siegenthaler et al., 2005

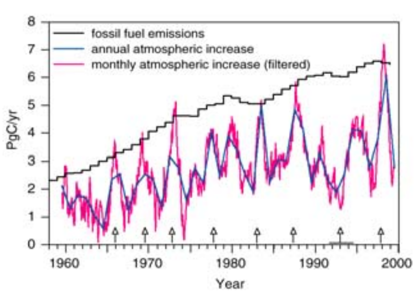
THE CURRENT CO_2 OBSERVATION NETWORK



RECENT GROWTH IN ATMOSPHERIC CO_2

Notice:

- **atmospheric increase is ~50% of fossil fuel emissions**
- **large interannual variability**



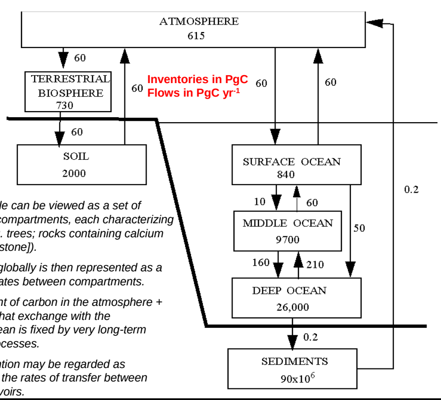
Arrows indicate El Nino events

GLOBAL CO_2 BUDGET (Pg C yr^{-1})

	1980s	1990s
Atmospheric increase	3.3 ± 0.1	3.2 ± 0.1
Emissions (fossil fuel, cement)	5.4 ± 0.3	6.3 ± 0.4
Ocean-atmosphere flux	−1.9 ± 0.6	−1.7 ± 0.5
Land-atmosphere flux*	−0.2 ± 0.7	−1.4 ± 0.7
**partitioned as follows:*		
Land-use change	*1.7 (0.6 to 2.5)*	*NA*
Residual terrestrial sink	*−1.9 (−3.8 to 0.3)*	*NA*

IPCC [2001]

GLOBAL PREINDUSTRIAL CARBON CYCLE



The carbon cycle can be viewed as a set of "reservoirs" or compartments, each characterizing a form of C (e.g. trees; rocks containing calcium carbonate [limestone]).

The cycle of C globally is then represented as a set of transfer rates between compartments.

The total amount of carbon in the atmosphere + ocean + rocks that exchange with the atmosphere/ocean is fixed by very long-term geophysical processes.

Human intervention may be regarded as manipulation of the rates of transfer between important reservoirs.

CARBON CYCLE ON LAND

- **Photosynthesis:**

$$CO_2 + H_2O + \text{light} \rightarrow \text{"}H_2CO\text{"} + O_2$$

- **Respiration:**

$$\text{"}H_2CO\text{"} + O_2 \rightarrow CO_2 + H_2O + \text{energy}$$

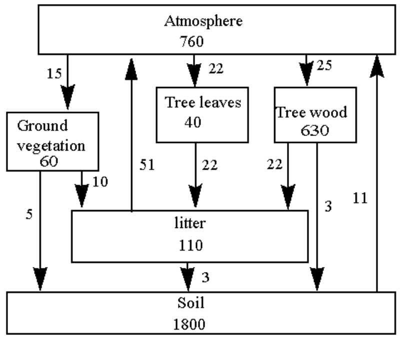
Very little organic matter is stored, on average.

CARBON CYCLE IN THE OCEAN

- **Dissolution/evasion**

$$CO_{2(g)} + H_2O + CO_{3(aq)}^{=} \Leftrightarrow 2\,HCO_3^-$$

CYCLING OF CARBON WITH TERRESTRIAL BIOSPHERE



Inventories in PgC
Flows in PgC yr^{-1}

Time scales are short ⇨ net uptake from reforestation is transitory

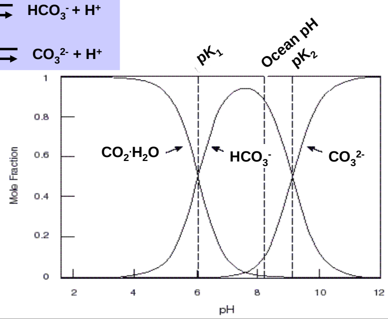
UPTAKE OF CO_2 BY THE OCEANS

ATMOSPHERE $CO_2(g)$

OCEAN $K_H = 3\times10^{-2}$ M atm^{-1} $CO_2{\cdot}H_2O$

$K_1 = 9\times10^{-7}$ M $CO_2{\cdot}H_2O \rightleftarrows HCO_3^- + H^+$

$K_2 = 7\times10^{-10}$ M $HCO_3^- \rightleftarrows CO_3^{2-} + H^+$

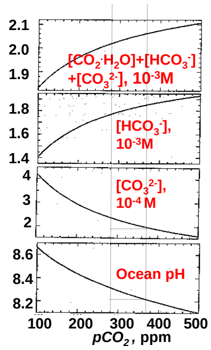


Net uptake:

$CO_2(g) + CO_3^{2-} \xrightarrow{H_2O}$

LIMIT ON OCEAN UPTAKE OF CO_2: CONSERVATION OF ALKALINITY

Equilibrium calculation
for Alk = 2.25×10^{-3} M



The alkalinity is the excess positive charge in the ocean to be balanced by carbon:

$$Alk = [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] - [Cl^-] - 2[SO_4^{2-}] - [Br^-]$$

$$= [HCO_3^-] + 2[CO_3^{2-}]$$

It is <u>conserved</u> upon addition of CO_2
⇨ uptake of CO_2 is limited by the existing supply of CO_3^{2-}

Increasing Alk requires dissolution of sediments:

$$CaCO_3 \rightleftarrows Ca^{2+} + CO_3^{2-}$$

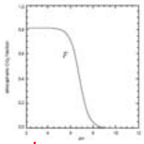
…which takes place over a time scale of thousands of years

EQUILIBRIUM PARTITIONING OF CO_2 BETWEEN ATMOSPHERE AND GLOBAL OCEAN

Fraction of CO_2 in atmosphere (Equilibrium for present-day ocean, pH=8.2):

$$F = \frac{N_{CO2}(g)}{N_{CO2}(g) + N_{CO2}(aq)} = 0.03$$

varies roughly as [H⁺]   moles



⇨ only 3% of total inorganic carbon is currently in the atmosphere

But $CO_2(g)$ ↗ ⇨ [H⁺] ↗ ⇨ *F* ↗
… *positive feedback to increasing CO_2*

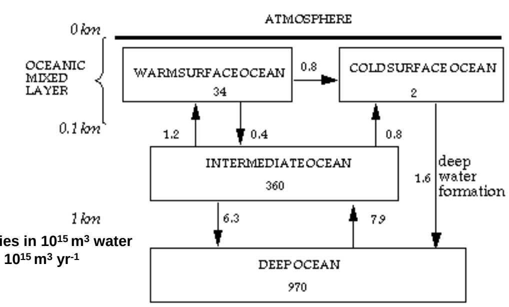
Pose problem differently: how does a CO_2 addition *dN* partition between the atmosphere and ocean at equilibrium?

$$f = \frac{dN_{CO2}(g)}{dN_{CO2}(g) + dN_{CO2}(aq)} =$$

varies roughly as $[H^+]^2$

⇨ 28% of added CO_2 remains in atmosphere! Reflects large positive feedback from ocean acidification by CO_2

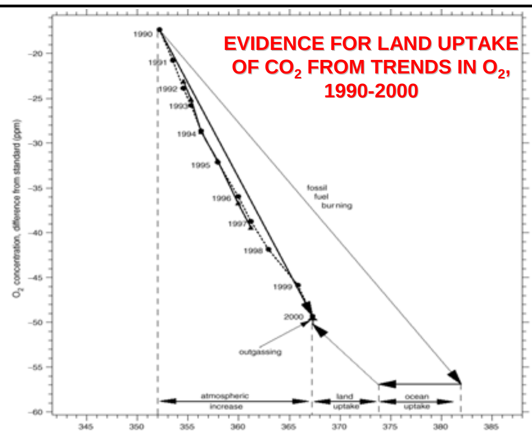
FURTHER LIMITATION OF CO_2 UPTAKE: SLOW OCEAN TURNOVER (~ 200 years)



Inventories in 10^{15} m³ water
Flows in 10^{15} m³ yr⁻¹

Uptake by oceanic mixed layer only (V_{OC}= 3.6x10^{16} m³) would give *f* = 0.94 (94% of added CO_2 remains in atmosphere)
Residence time of water in the oceanic mixed layer is ~18 years.

EVIDENCE FOR LAND UPTAKE OF CO_2 FROM TRENDS IN O_2, 1990-2000



QUESTIONS

1. There is concern that melting of polar icecaps could reduce deep water formation and hence the transfer of CO_2 to the deep ocean. Why? (Hint: temperature is not the only factor driving deep water formation)

2. Upwelling of deep ocean water supplies high concentrations of nutrients such as nitrogen to the surface ocean. What is the effect of this upwelling on atmospheric CO_2?

3. Former Alberta Premier Ralph Klein suggested that we all quit breathing as a way to reduce CO_2 input to the atmosphere. Jamey Heath, a spokesman for Greenpeace Canada, called it the "single stupidest argument" he had ever heard against ratifying Kyoto. Who's right? Why?