Carbon isotope mass balance modelling of atmospheric vs. oceanic CO_2

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Asserted rise in atmospheric CO_2

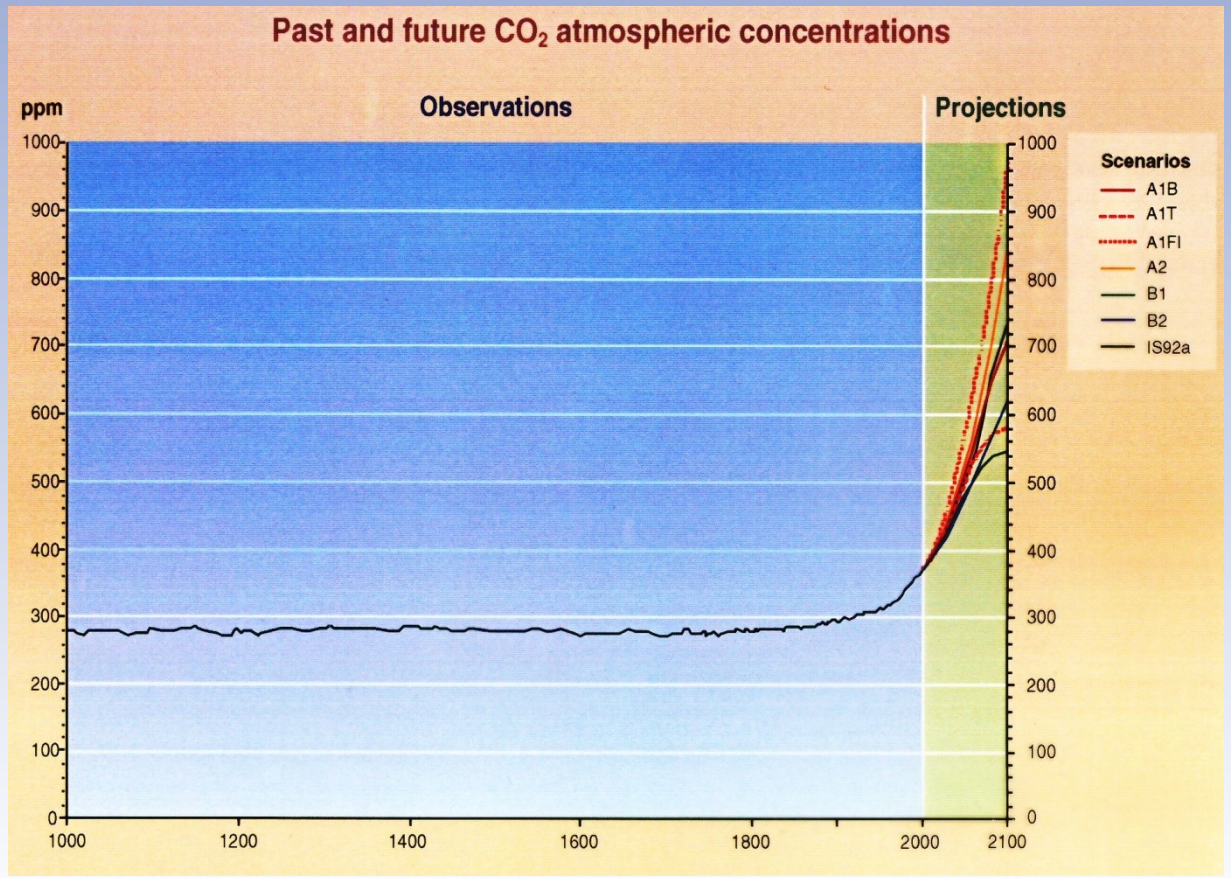
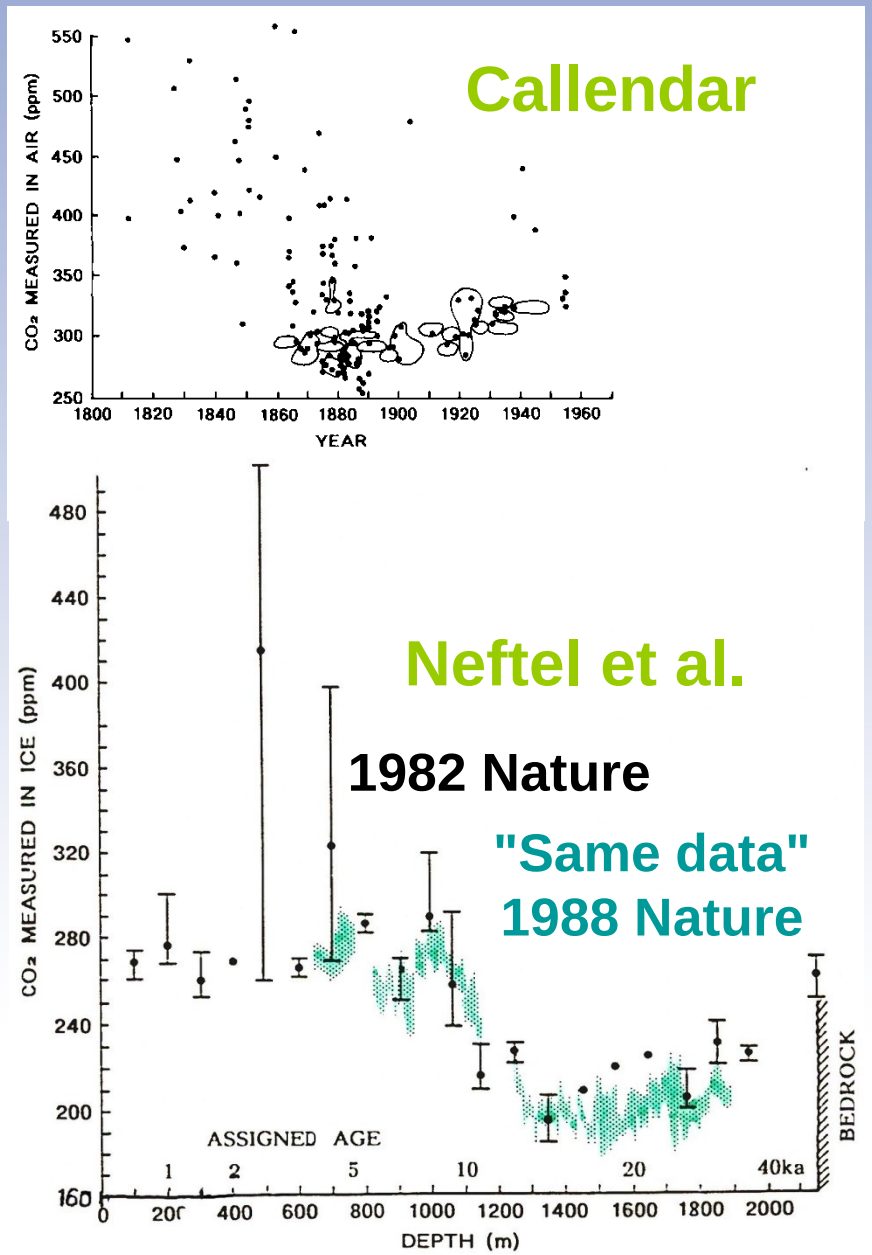


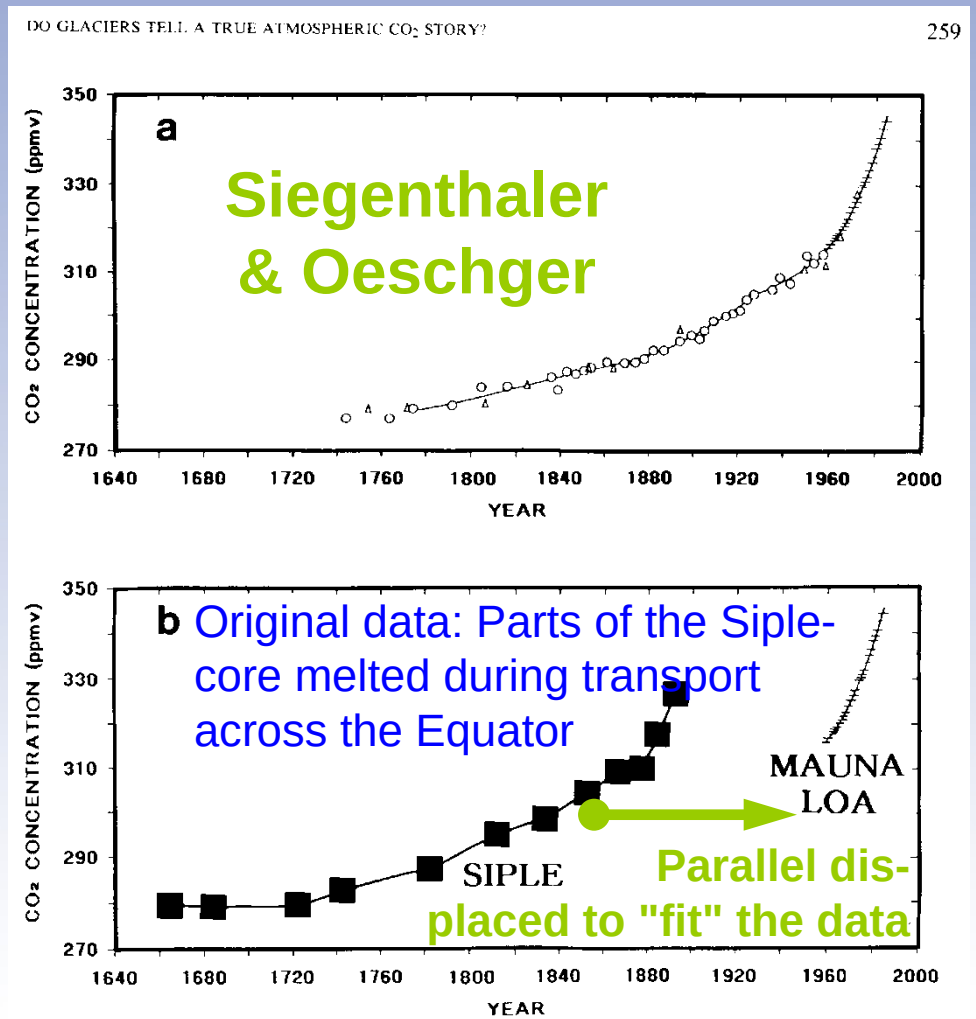
Illustration from IPCC TAR 2001

The Intergovernmental Panel on Climate Change (IPCC) asserts that the burning of fossil fuel makes this anthropogenic CO_2 accumulate in the Earth's atmosphere, because this CO_2 has a long lifetime, up to 200 years (*"rough indication 50 – 200 years"*). This assertion will here be tested with C isotopes.

Pre-industrial CO_2 level?

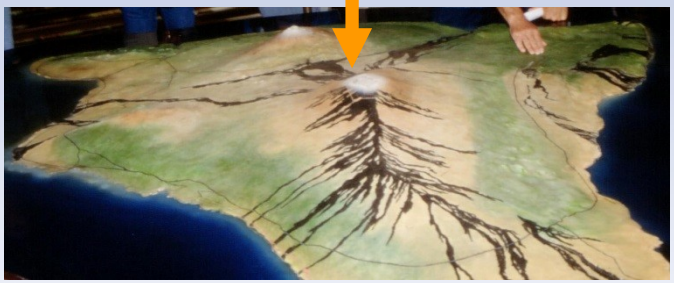
From: Jaworowski, Segalstad & Ono (1992): *Science of the Total Environment 114*, 227-284.

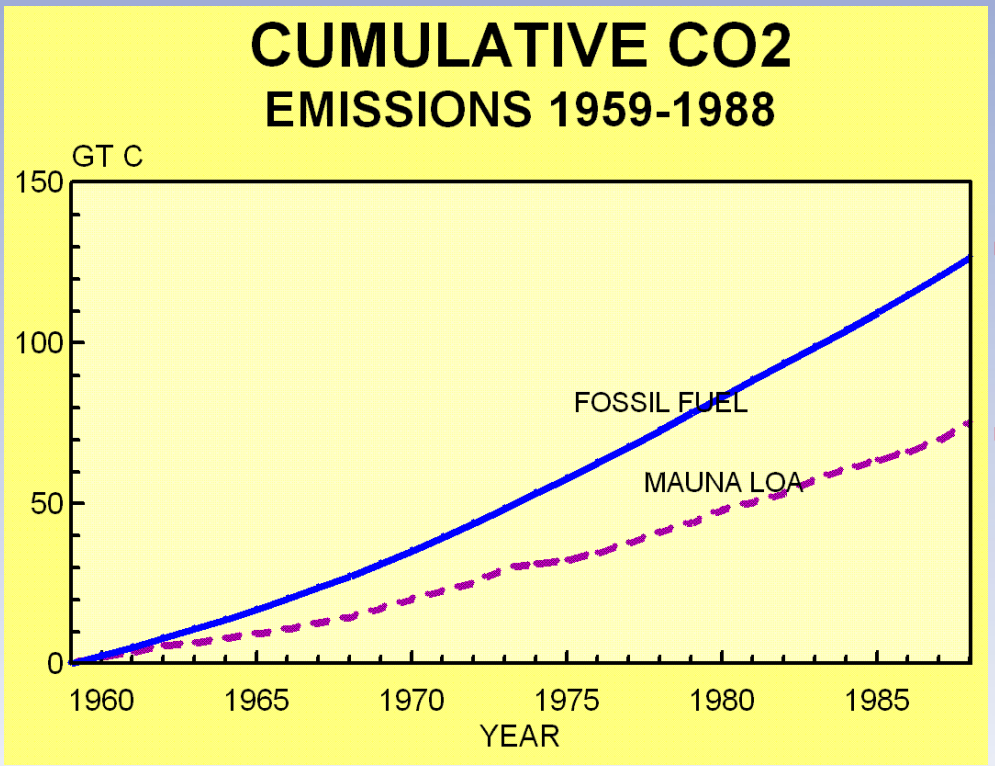




IPCC assumed a pre-industrial CO_2 value of 280 ppmv in air based on selected low values from ice cores, ignoring numerous wet-chemical analyses of CO_2 in air.

Cumulative CO_2 emissions

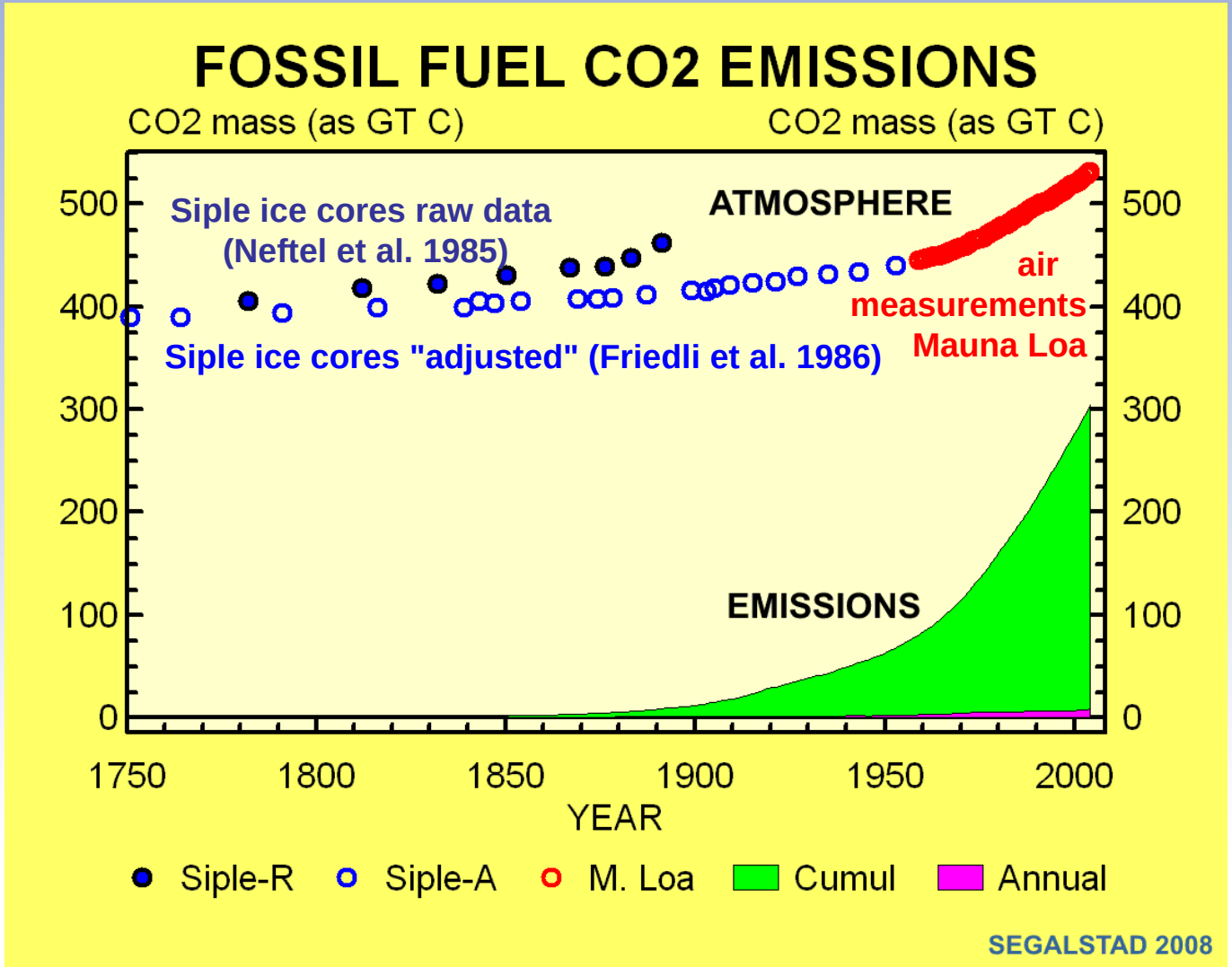




CO_2 measurements near the top of the strongly CO_2-emitting active volcano **Mauna Loa** in Hawaii have been taken as representative of the world's air CO_2 level. There is a ***~50% error*** vs. the expected CO_2 level from burning fossil fuel. This enormous error of 3 – 4 GT C annually has been nicknamed ***"The Missing Sink"***, and disproves the IPCC.

Accumulated CO_2 emissions 1750 – today

in atmospheric CO_2 computed from Marland et al. 2007



The diagram shows that anthropogenic emissions of CO_2 from burning of fossil fuels ***cannot*** be the reason for the increase in atmospheric CO_2.

Stable carbon isotopes

Carbon isotopes give us the only way to unequivocally determine the fraction of CO_2 in the atmosphere.

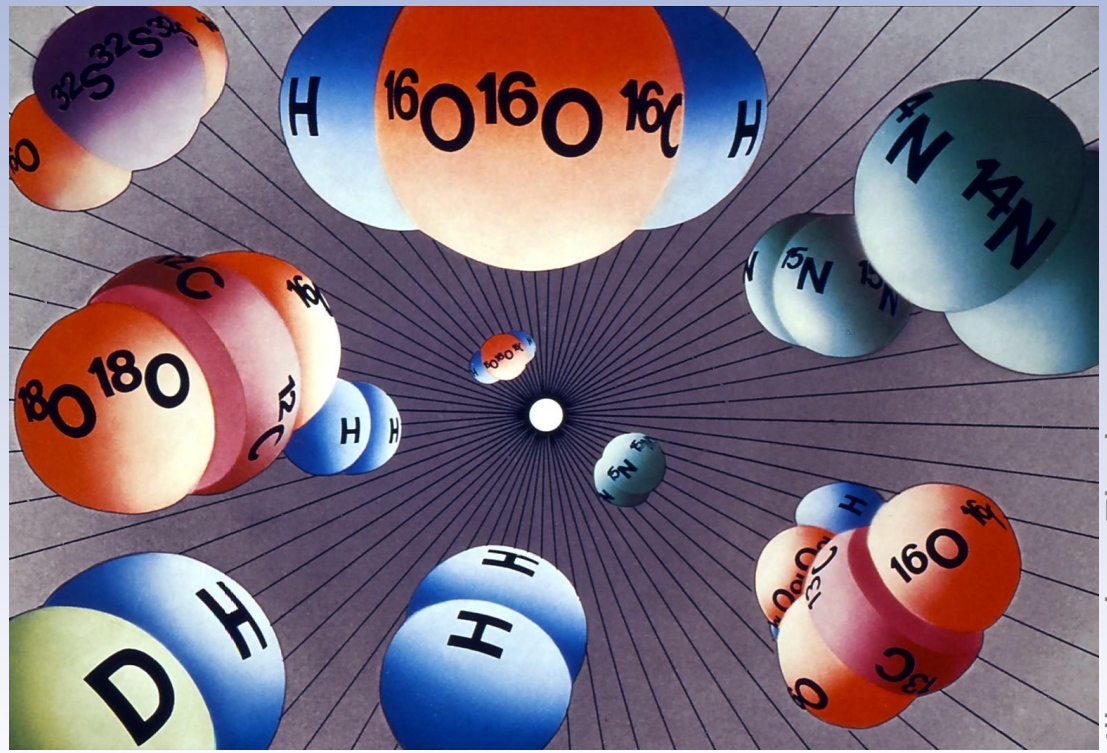
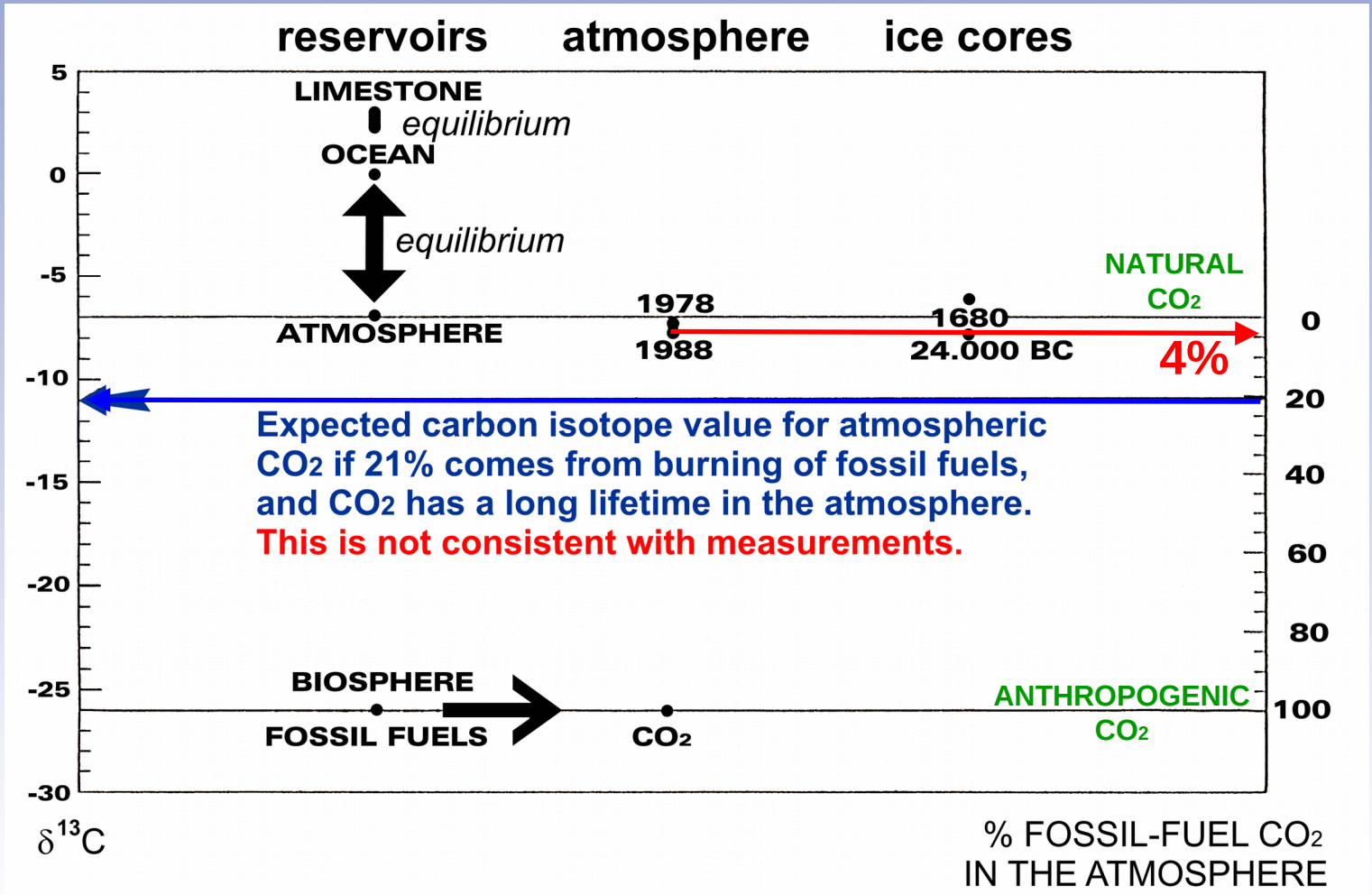


Illustration: Finnigan

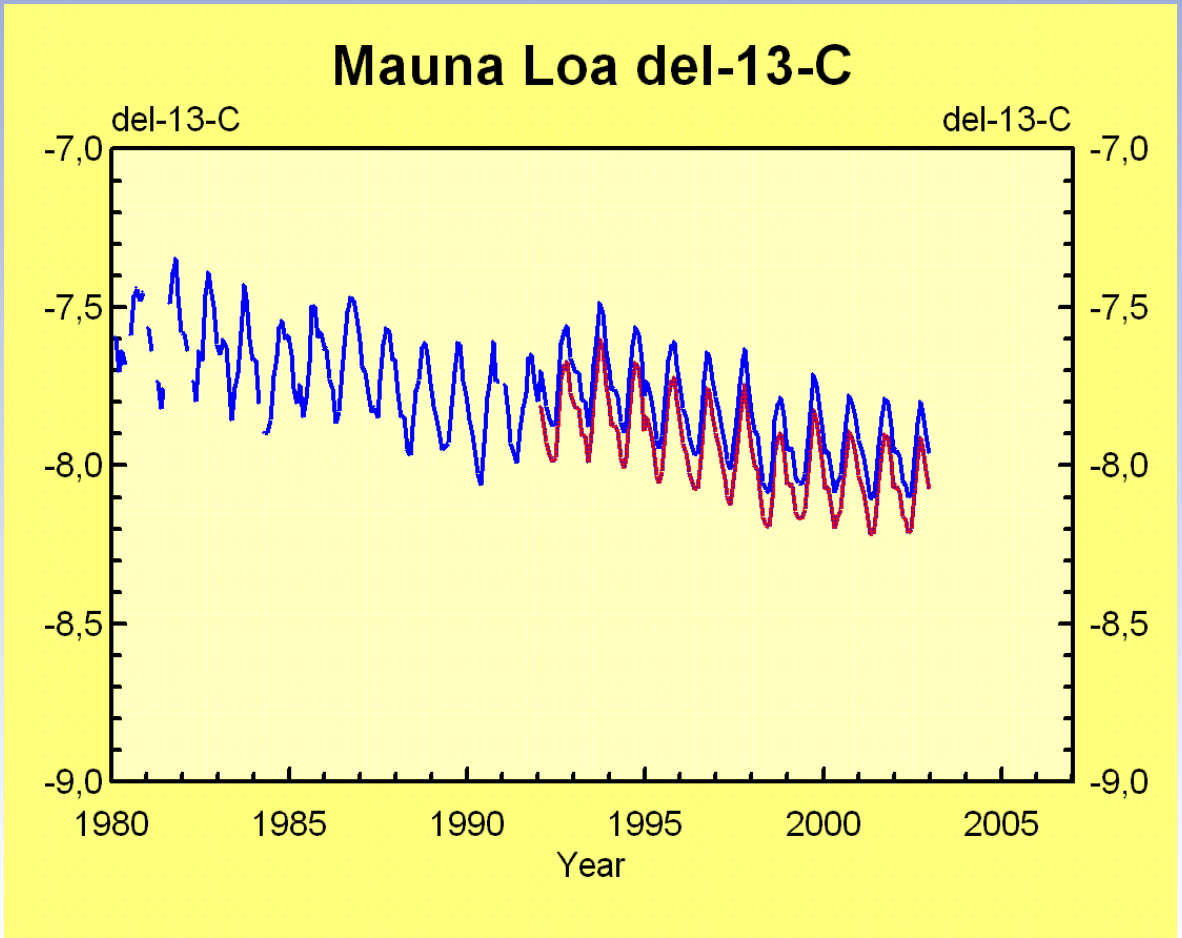
$^{13}C/^{12}C$ isotope ratios are expressed as δ (delta) values defined as the standard-normalized difference from the standard, expressed as $\delta^{13}C$ in per mil (‰). The reference standard used is PDB (Pee Dee Belemnite).

Proof from stable carbon isotopes



Left: reservoirs found to be in carbon isotopic equilibrium. Burning of biospheric fossil fuel adds ^{12}C (low $\delta^{13}C$) to the air. $\delta^{13}C$ of air in 1988 shows ~4% anthropogenic CO_2 in air (right scale shows % mixing). Not 21% as asserted by the IPCC, which would have given air $\delta^{13}C \approx -11$.

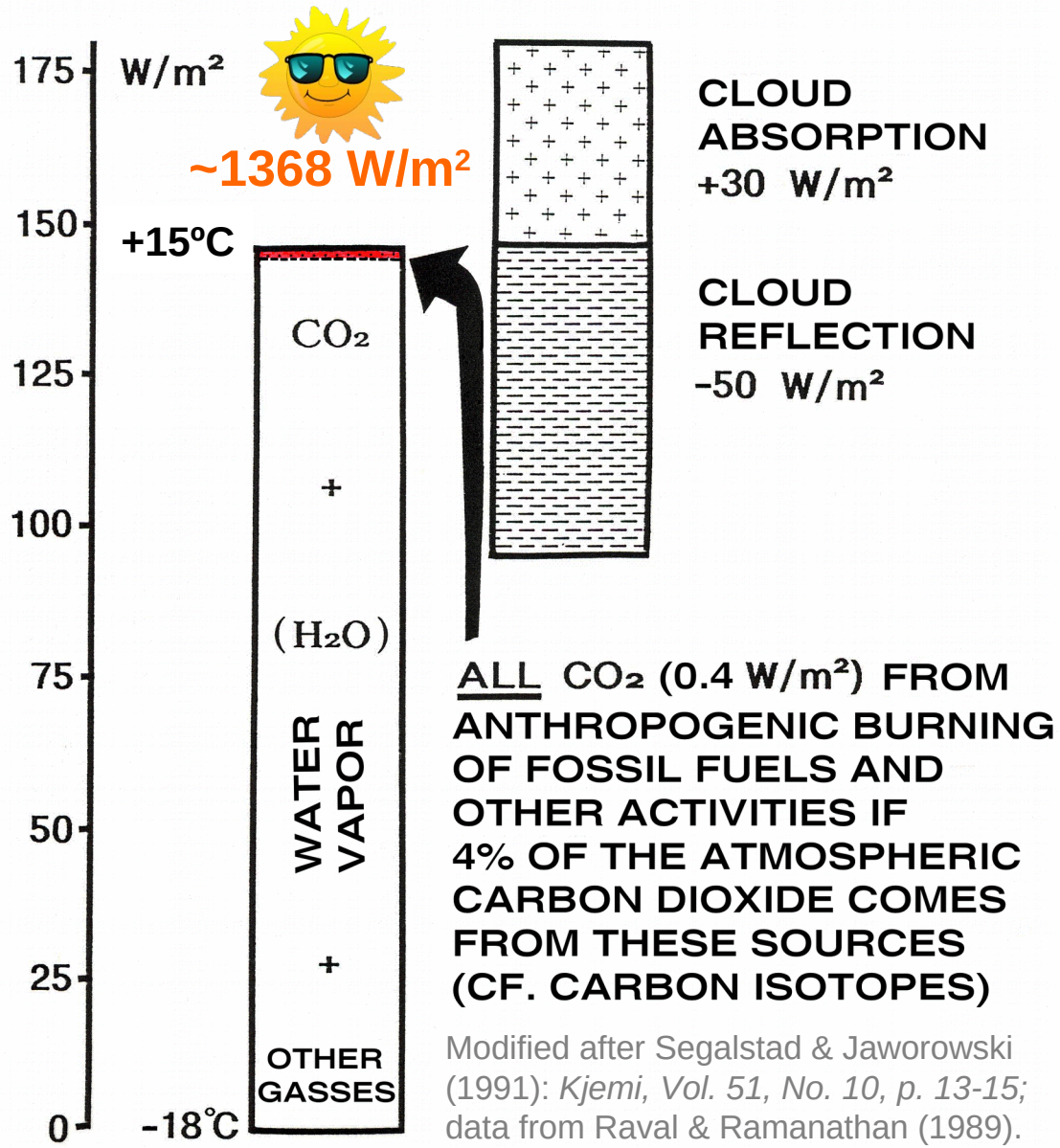
Carbon isotope record



$^{13}C/^{12}C$ carbon isotope data as $\delta^{13}C$ in ‰ by Keeling et al. 2005:
http://cdiac.esd.ornl.gov/trends/co2/iso-sio/iso-sio.html
The raw data (blue) has been *"adjusted"* from Jan. 1992 by lowering them by -0.112‰ according to the authors (red curve).

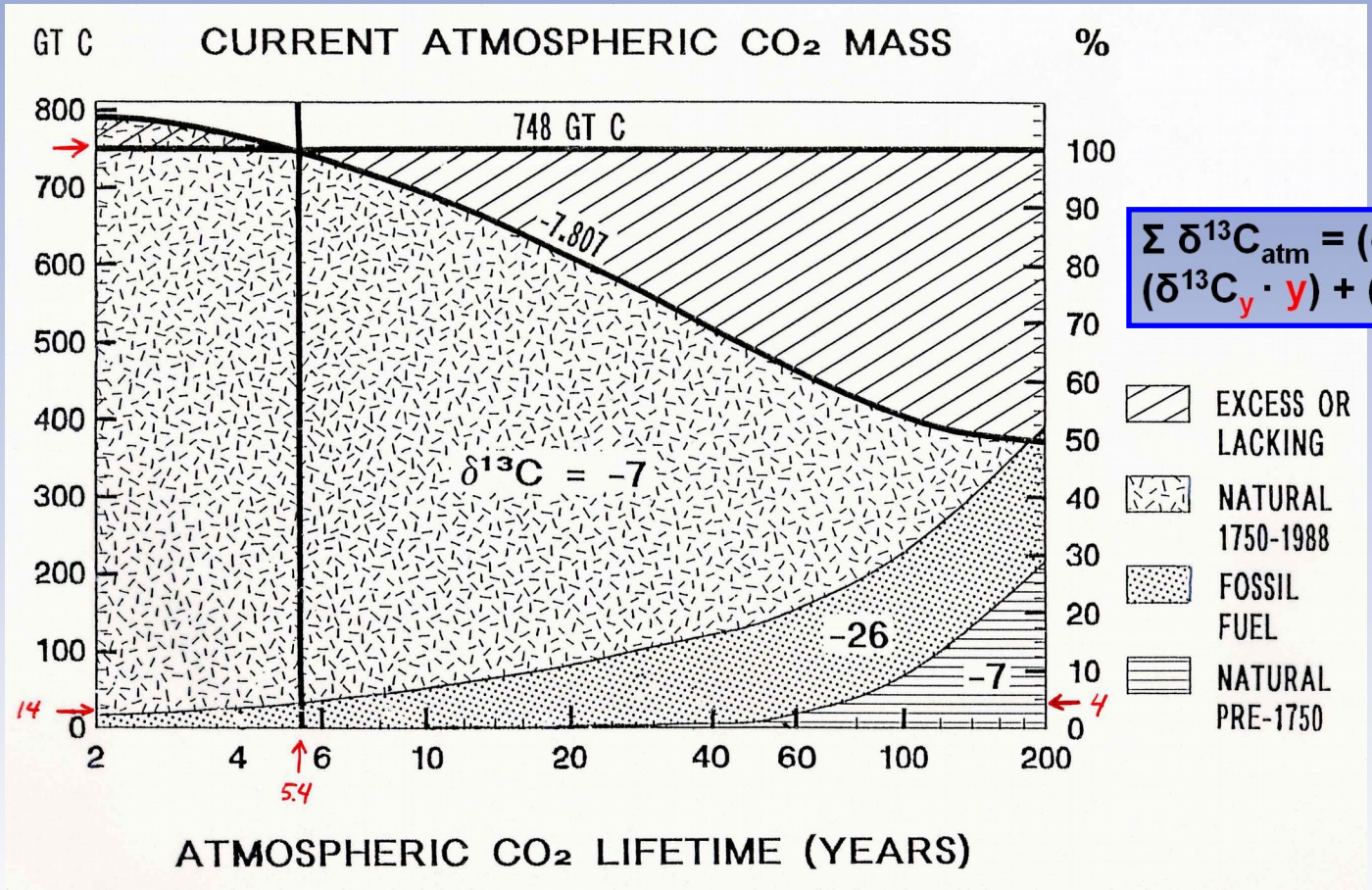
Energy relations

Some of the trace gasses in air can absorb heat, making the Earth habitable (~ +15°C vs. minus 18°C) by the *"Greenhouse Effect"*, 146 W/m² of cloud-free air, ~98% dominated by ***water vapor***. Anthropogenic CO_2 is less than ½ W/m², less than 0.1%, judged from the *C isotopes*. ***Clouds*** are the real thermostat, with far more temperature regulating power than CO_2.



Modified after Segalstad & Jaworowski (1991): *Kjemi, Vol. 51, No. 10, p. 13-15;* data from Raval & Ramanathan (1989).

Proof from isotopic mass balance



$$\Sigma\, \delta^{13}C_{atm} = (\delta^{13}C_x \cdot x) + (\delta^{13}C_y \cdot y) + (\delta^{13}C_z \cdot z)$$

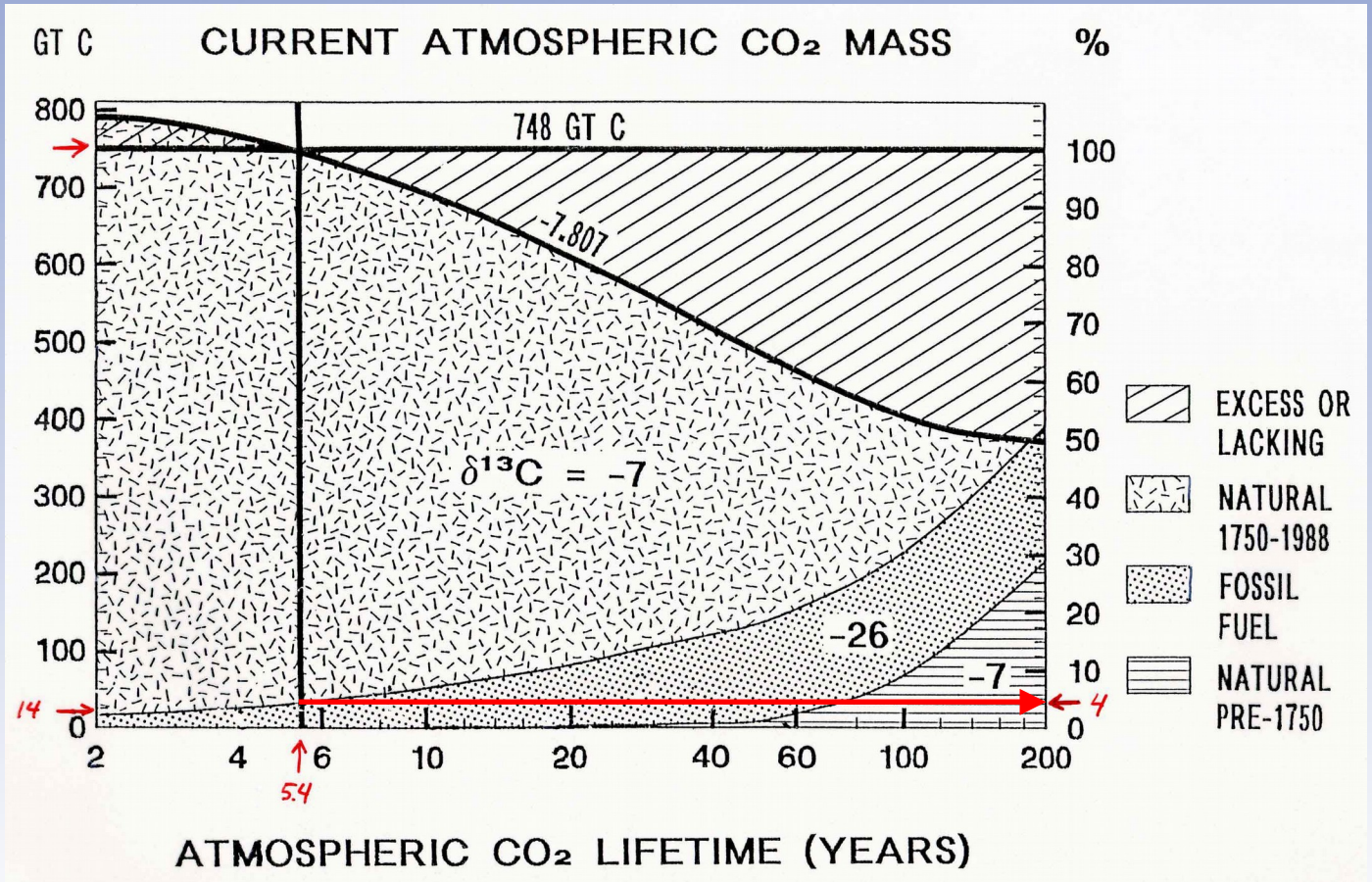
x

y

z

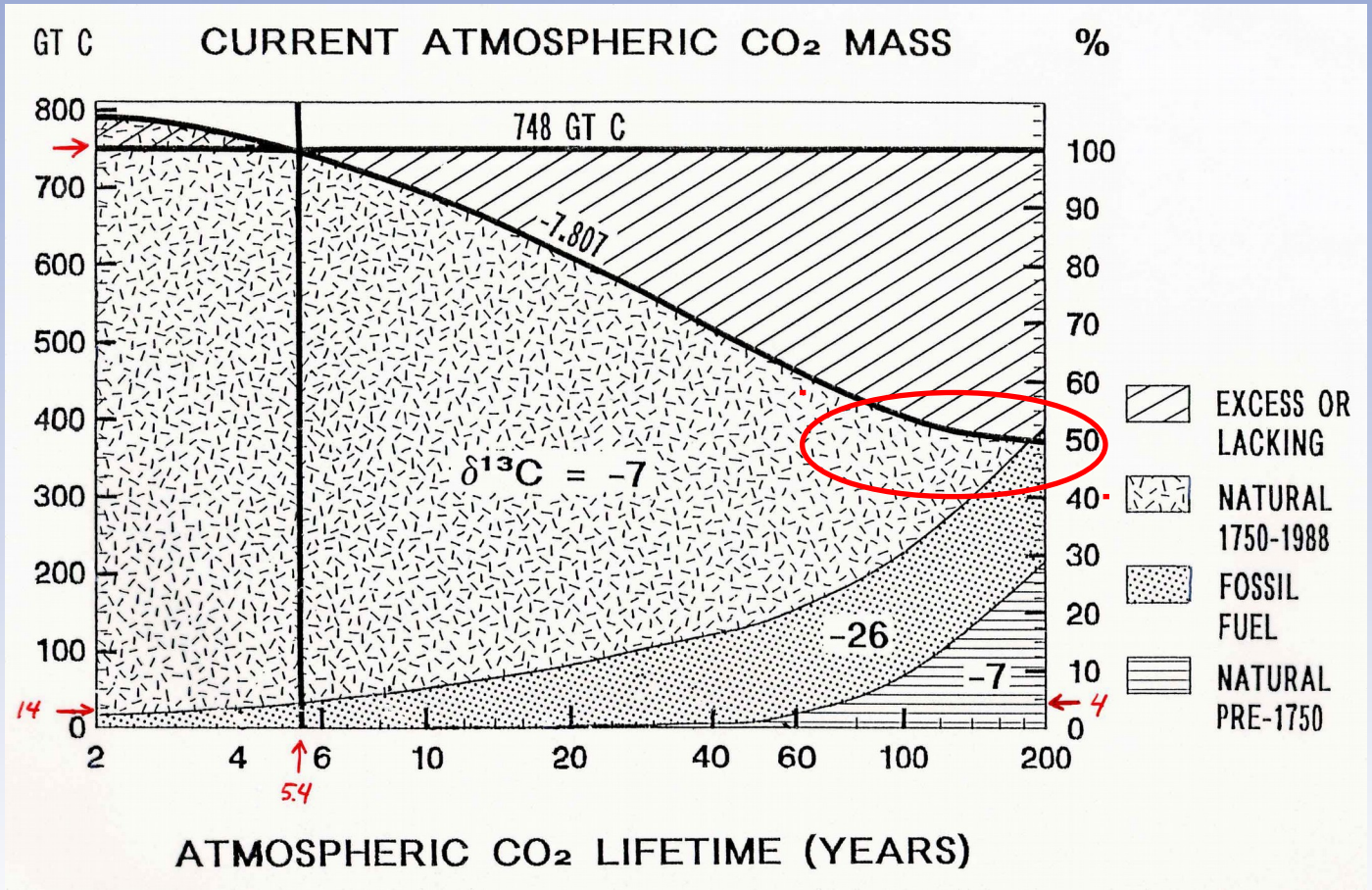
Using the radioactive decay equation for the lifetime of CO_2 in air, we can calculate the masses of remaining CO_2 from different reservoirs using isotopic mass balance; checking for match vs. air CO_2 in December 1988: mass = 748 GT C; $\delta^{13}C$ = -7.807 (Keeling et al. 1989).

Proof from isotopic mass balance



The calculations confirm that maximum **4%** (14 GT C) of the air CO_2 has anthropogenic origin; **96%** is indistinguishable from non-fossil-fuel (natural marine and juvenile) sources. Air CO_2 lifetime is **~5 years**. ~134 GT C (18%) of air CO_2 is exchanged each year, **far more** than the ~7 GT C annually released from fossil fuel burning.

Proof from isotopic mass balance



We also see why the IPCC's *"rough indication"* lifetime 50-200 years for atmospheric CO_2 gives an atmosphere which is too light; only 50% of the atmospheric CO_2 mass. This may explains why a wrong model creates the artificial 50% error, nicknamed *"The Missing Sink"*.

Effective atmospheric CO_2 lifetime

The effective lifetime for CO_2 in the atmosphere, can be determined by the help of radioactive, radiogenic, and stable isotopes.

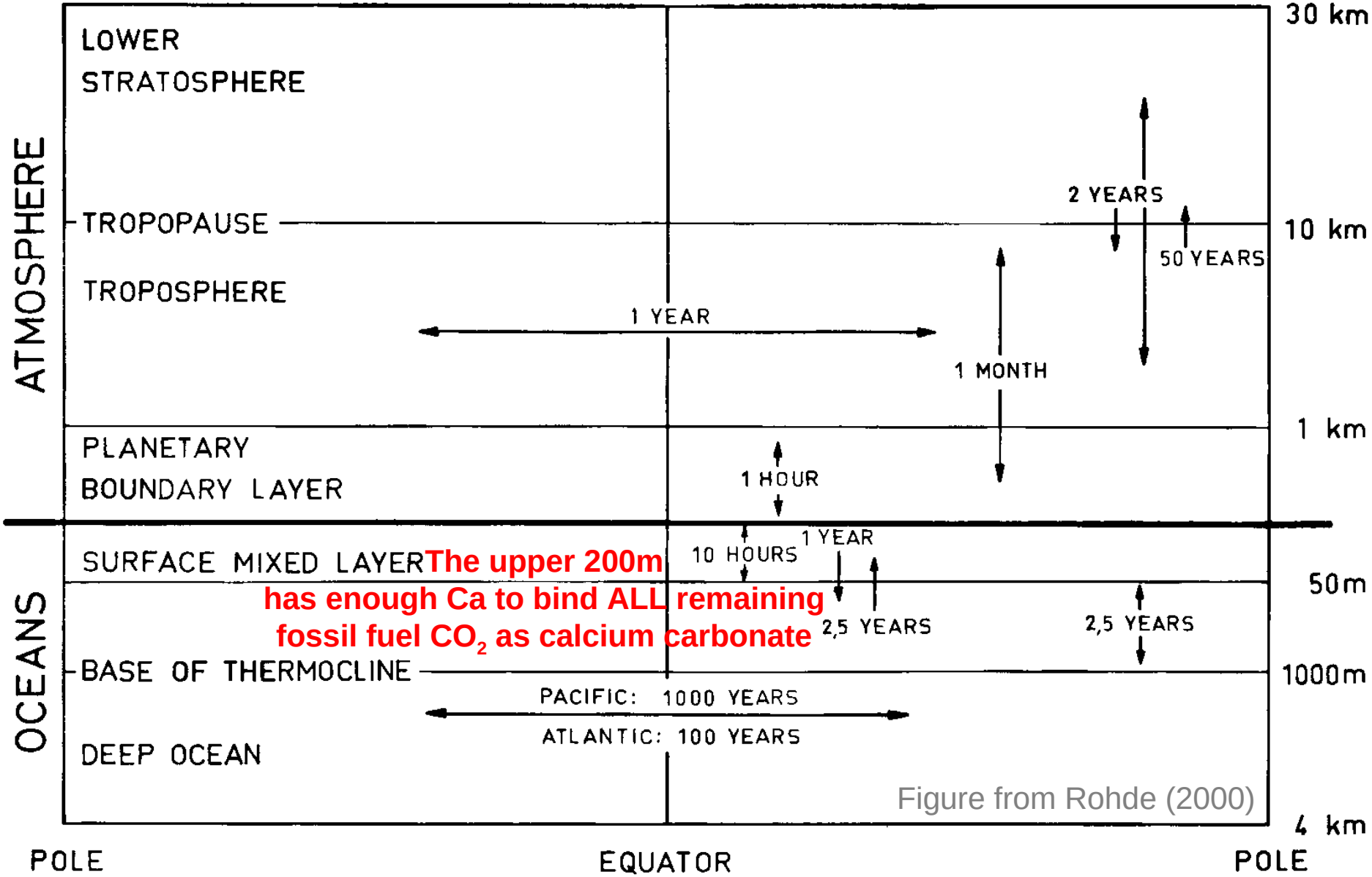
Authors [publication year]	Residence time (years)
Based on natural carbon-14	
Craig [1957]	7 +/- 3
Revelle & Suess [1957]	7
Arnold & Anderson [1957]	10
including living and dead biosphere (Siegenthaler, 1989)	4-9
Craig [1958]	7 +/- 5
Bolin & Eriksson [1959]	5
Broecker [1963], recalc. by Broecker & Peng [1974]	8
Craig [1963]	5-15
Keeling [1973b]	7
Broecker [1974]	9.2
Oeschger et al. [1975]	6-9
Keeling [1979]	7.53
Peng et al. [1979]	7.6 (5.5-9.4)
Siegenthaler et al. [1980]	7.5
Lal & Suess [1983]	3-25
Siegenthaler [1983]	7.9-10.6
Kratz et al. [1983]	6.7
Based on Suess Effect	
Ferguson [1958]	2 (1-8)
Bacastow & Keeling [1973]	6.3-7.0
Based on bomb carbon-14	
Bien & Suess [1967]	>10
Münnich & Roether [1967]	5.4
Nydal [1968]	5-10
Young & Fairhall [1968]	4-6
Rafter & O'Brian [1970]	12
Machta (1972)	2
Broecker et al. [1980a]	6.2-8.8
Stuiver [1980]	6.8
Quay & Stuiver [1980]	7.5
Delibrias [1980]	6.0
Druffel & Suess [1983]	12.5
Siegenthaler [1983]	6.99-7.54
Based on radon-222	
Broecker & Peng [1974]	8
Peng et al. [1979]	7.8-13.2
Peng et al. [1983]	8.4
Based on solubility data	
Murray (1992)	5.4
Based on carbon-13/carbon-12 mass balance	
Segalstad (1992)	5.4

All measurements with different methods show short effective lifetimes for atmospheric CO_2, only ca.

5 - 6 years.

Sundquist (1985); Segalstad (1998)

Exchange time CO_2 air–water



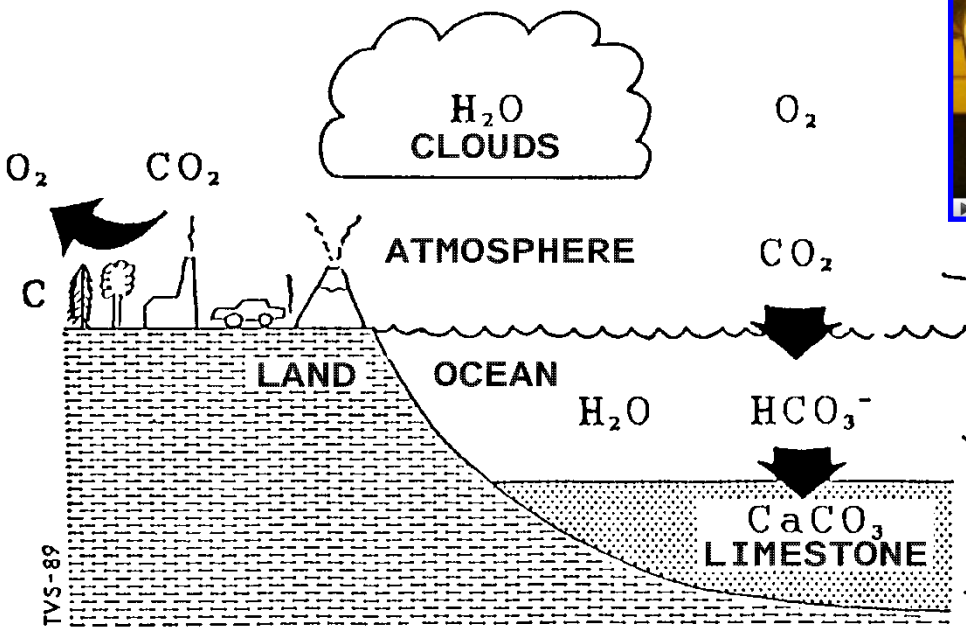
The upper 200m has enough Ca to bind ALL remaining fossil fuel CO_2 as calcium carbonate

Figure from Rohde (2000)

The inorganic carbon cycle

This is important: IPCC's ocean is clean, distilled water!
CO_2 enters the atmosphere from many sources to the left.
CO_2 from air dissolves, hydrolyses and protolyses in the sea.
CO_2 may combine with calcium and **precipitates as $CaCO_3$** (limestone) on the sea-floor with lime-shells from organisms.
Analogous to the *breathing of CO_2* into a test-tube with Ca^{2+} ions, where $CaCO_3$ precipitates almost instantaneously.

Video: http://www.youtube.com/watch?v=sjxUwDTkd4g



Segalstad, Aftenposten 1989

CO_2 and volcanism

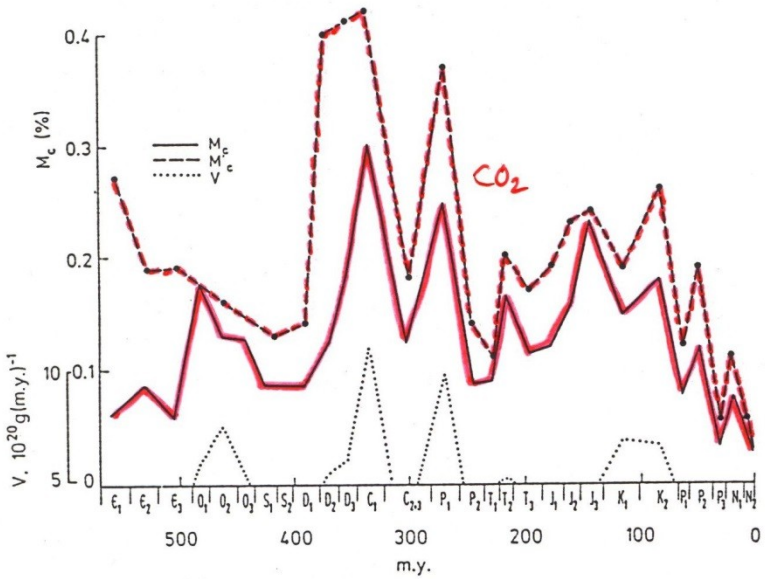


Fig. 24. Changes in carbon dioxide concentration (M_c, M'_c) and the rate of formation of volcanic rocks (V) during the Phanerozoic

Budyko et al. (1987)

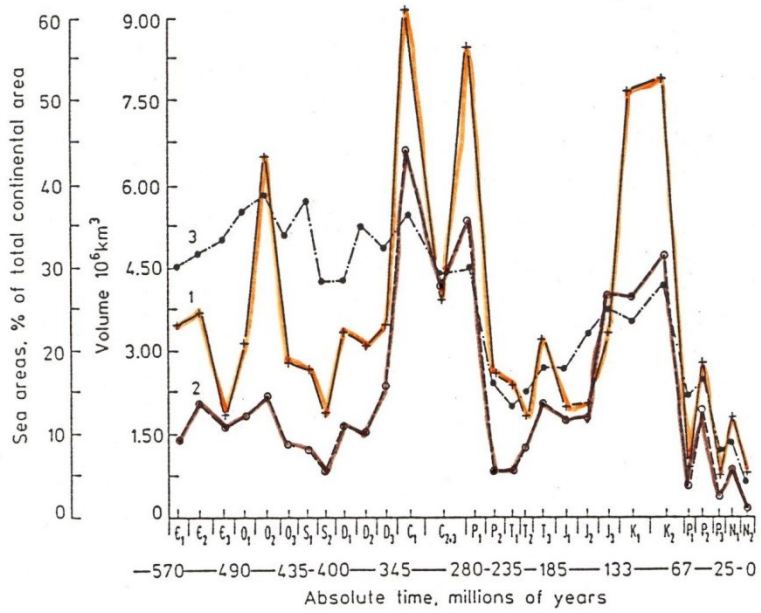
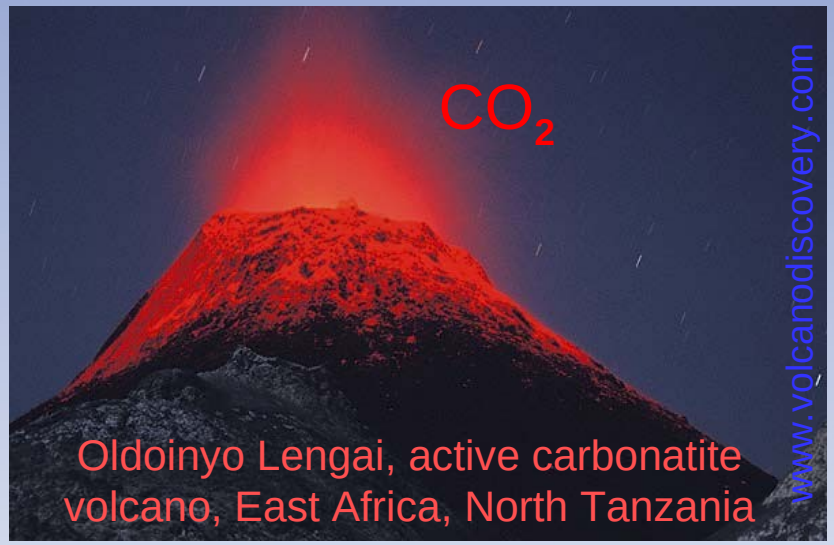
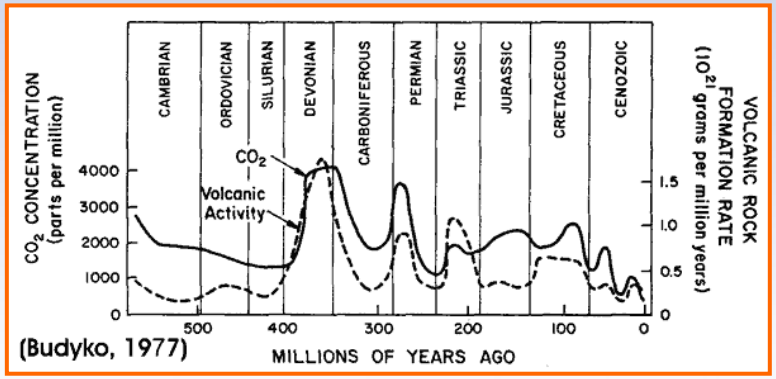


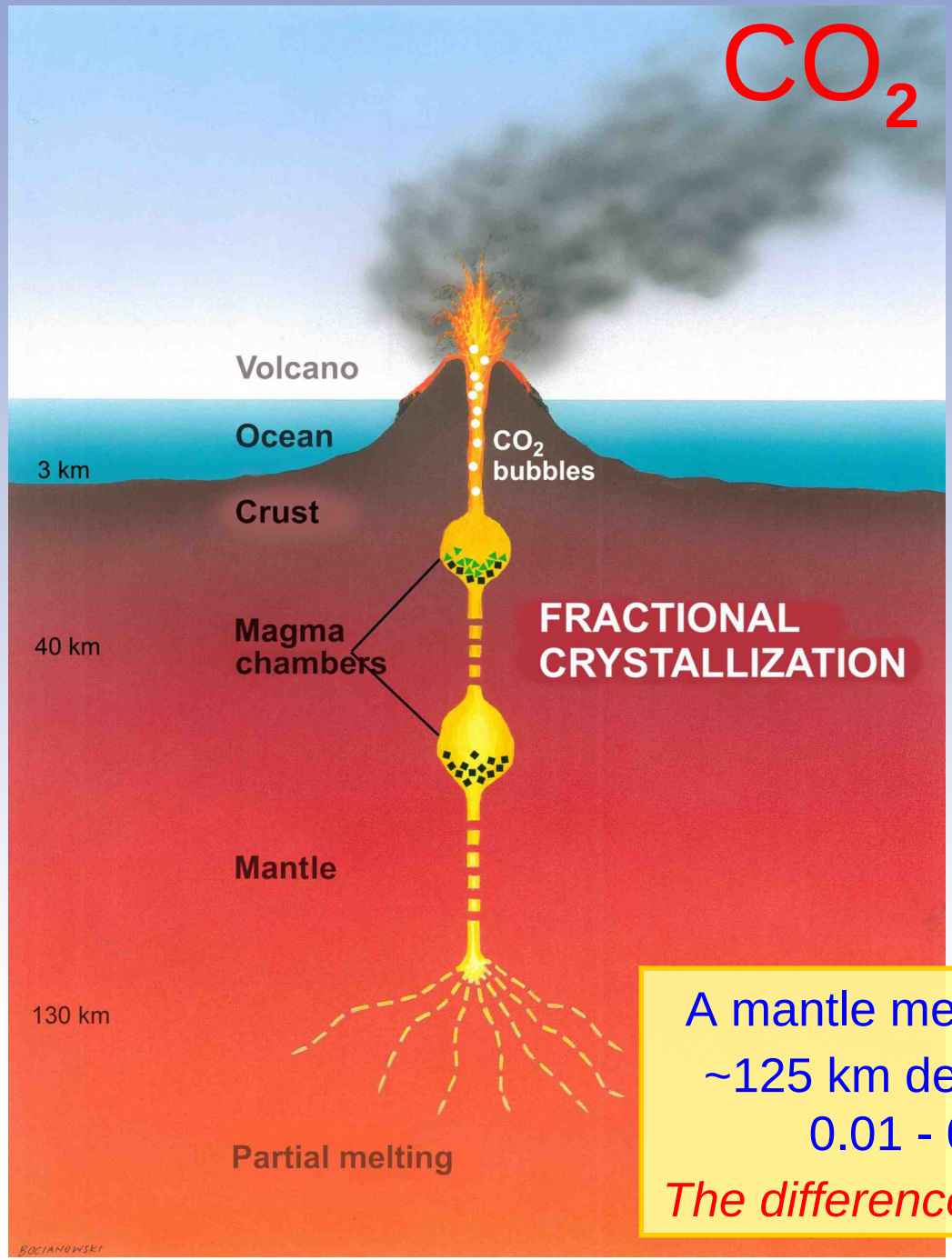
Fig. 14. Time changes in volcanogenic rock volumes (1), CO_2 buried in synchronous carbonate rocks (2) and the ratio (%) of the continental sea area to the total area of the continents (3)

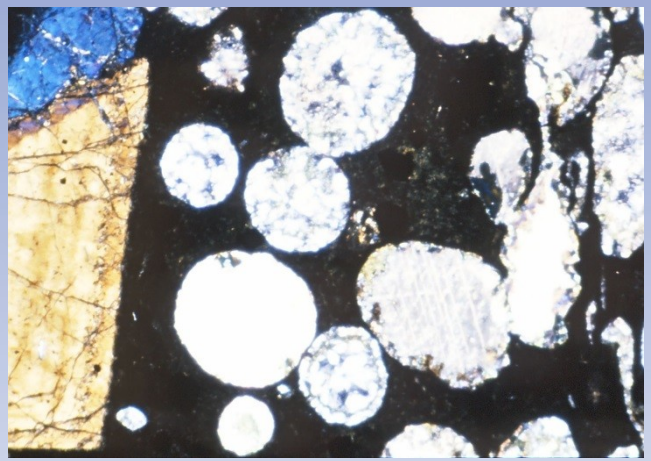




Mikhail I. Budyko has shown good correlation between emissions of CO_2 through periodes of extensive **volcanism** and deposition of **marine carbonate rocks** during the Earth's last ~600 million years.

CO_2 and volcanism





Immiscible magma-carbonate in nephelinite, Skien, Oslo Rift. Photo length 1.5 cm, polarized light. *Large amounts of CO_2 will be emitted during eruption!*

Segalstad, *Lithos, Vol.12*, 1979; Anthony, Segalstad & Neumann, *Geochimica Cosmochimica Acta, Vol.53*, 1989

A mantle melt may have up to 8 wt.% CO_2 at ~125 km depth. Surface lava can only hold 0.01 - 0.001 wt.% CO_2 dissolved.

The difference is degassed to the atmosphere!

CO_2 and volcanism

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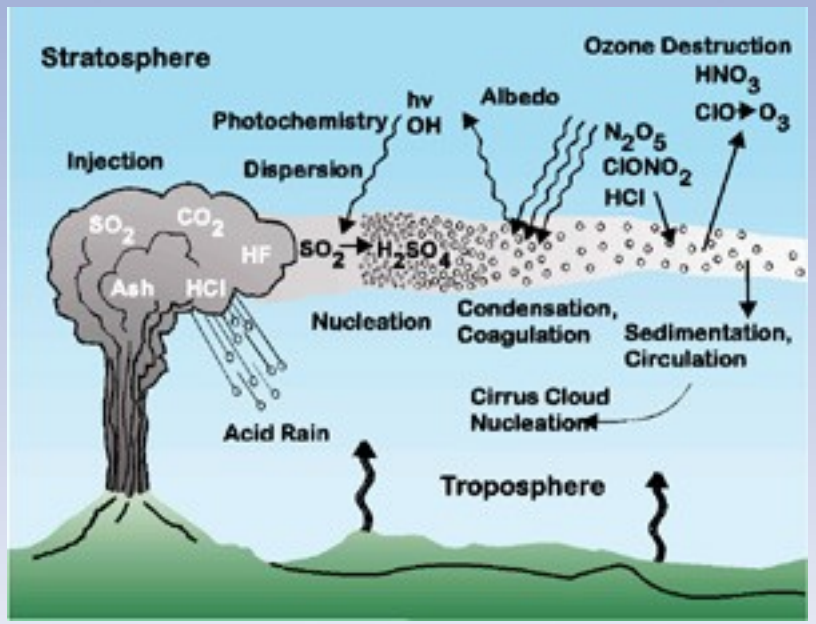
CO2 Degassing at Kilauea Volcano: Implications for Primary Magma, Summit Reservoir Dynamics, and Magma Supply Monitoring

Gerlach, T. M.; McGee, K. A.; Elias, T.; Sutton, A. J.; Doukas, M. P.

American Geophysical Union, Fall Meeting 2001, abstract #V22E-10

We report a new CO2 emission rate of 8,500 tons/day (t/d) for the summit of Kilauea Volcano, a result several times larger than previous estimates. It is based on 12 experiments on three occasions over four years constraining the SO2 emission rate and the average CO2/SO2 of emissions along the 5.4-km summit COSPEC traverse (by COSPEC, NDIR CO2 analyzer, and CP-FTIR). The core of the summit plume is at ground level along the traverse and gives average CO2/SO2 values that are representative of the overall summit emission, even though CO2 and SO2 variations are commonly uncorrelated. CO2 and SO2 concentrations exceed background by 200-1,000 ppm and 1-7 ppm respectively. Nighttime measurements exclude Park auto exhaust as a source of CO2. The summit CO2 emission rate is nearly constant (95% confidence interval = 300 t/d), despite variable summit SO2 emission rates (62-240 t/d) and CO2/SO2 (54-183). Including other known CO2 emissions on the volcano (mainly from the Pu`u `O`o eruption) gives a total emission rate of about 8,800 t/d. Thus summit CO2 emissions comprise 97% of the total known CO2 output, consistent with the hypothesis that all primary magma supplied to Kilauea arrives under the summit caldera and is thoroughly degassed of excess CO2. A persistent large CO2

CO_2 AND VOLCANISM



USGS

http://erebus.nmt.edu/geochemistry.php?page=Gas%20Chemistry

Kyle et al. (2008)

Table 2. Volcanic CO2 Emissions

Volcano	CO2 Flux (tonnes per day)	Percent from soil degassing	CO2/CO average value*
Mt. Etna	70,000	XXX	47.9
	11-38,000		
Popocatepetl	6,400	0	- -
	40,000		
Oldoinyo Lengai	7,200	<2	- -
Augustine	6,000	- -	- -
Mt. St. Helens	4,800	- -	401
Stromboli	3,000	- -	- -
Kilauea	~~2,800~~ 8,800	~50	30.8
White Island	2,600	<1	6825
Erebus	1850	- -	12.3
Redoubt	1800	- -	- -
Grimsvotn	360	- -	- -
Vulcano	270	20	413

* The values presented are averages taken from data by Symonds et al., 1994.

Data sources for available CO2 emissions: Gerlach et al., 1997; Allard et al., 1998; Varley et al., 1998; Delagdo et al., 1998; Kopenick et al., 1996; Allard et al., 1994; Wardell and Kyle, 1998; Brantley et al., 1993; and O'Keefe, 1994.

If each of the 1511 active land-volcanoes (cf. *"Volcanoes of the World"*) on Earth emits 5.000 tons C-equivalents of CO_2 each day => 7,5 million tons per day. *If* 4 times more from subaerial volcanoes => 37,5 Mtons total, ***approx. the double amount*** vs. burning of fossil fuels (<20 Mtons per day).

New threat: *acidification* of the oceans?

2008:

Second Symposium on the Ocean in a High-CO_2 World

The Scientific Committee on Oceanic Research,
the Intergovernmental Oceanographic Commission of UNESCO,
the International Atomic Energy Agency,
and the International Geosphere-Biosphere Programme
are planning a second Symposium
on the Ocean in a High-CO_2 World.

International Council for Science
Scientific Committee on Oceanic Research

UNESCO

IAEA

GLOBAL CHANGE
IGBP

How strange: Even if IPCC asserts that only ***slight*** CO_2 will dissolve in the ocean, this ***trifle amount*** of CO_2 will make a ***catastrophy*** by *dissolving all calcium carbonate in the sea!* This assertion can be *tested* by *data & thermodynamics …*

CO_2 equilibria air – ocean – $CaCO_3$

$CO_2\ (g) \leftrightarrow CO_2\ (aq)$	*dissolution*
$CO_2\ (aq) + H_2O \leftrightarrow H_2CO_3\ (aq)$	*hydrolysis*
$H_2CO_3\ (aq) \leftrightarrow H^+ + HCO_3^-\ (aq)$	*1st protolysis*
$HCO_3^-\ (aq) \leftrightarrow H^+ + CO_3^{2-}\ (aq)$	*2nd protolysis*
$Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \leftrightarrow CaCO_3\ (s)$	*precipitation*
$2\ H^+ + 2\ OH^- \leftrightarrow 2\ H_2O$	*protolysis*

$CO_2\ (g) + Ca^{2+}\ (aq) + 2\ OH^- \leftrightarrow CaCO_3\ (s) + H_2O$ ***net reaction***

Note that increase in **CO_2 (g)** will force the reaction to the right.

Equilibria are governed by the Law of Mass Action + **Henry's Law**:
The partial pressure of CO_2 (g) in air is proportional to the concentration of CO_2 (aq) dissolved in water.
The proportionality constant is **Henry's Law Constant**, **K_H**; strongly dependent on temperature, less on pressure and salinity.

Henry's Law in daily use

Henry's Law Constant is an equilibrium partition coefficient for CO_2 (g) in air vs. CO_2 (aq) in water:

at 25°C $K_H \approx 1 : 50$

At lower temperature more gas dissolves in the water.

We have all experienced this – cold soda or beer or champagne can contain more CO_2; thus has more effervescense than hot drinks.

The brewery sais that they add 3 liters of CO_2 to 1 liter of water in the soda. *But where did all the CO_2 go?*

Henry's Law in daily use

Henry's Law Constant directs that CO_2 (g) in air vs. CO_2 (aq) in water at 25°C is distributed ≈ 1 : 50

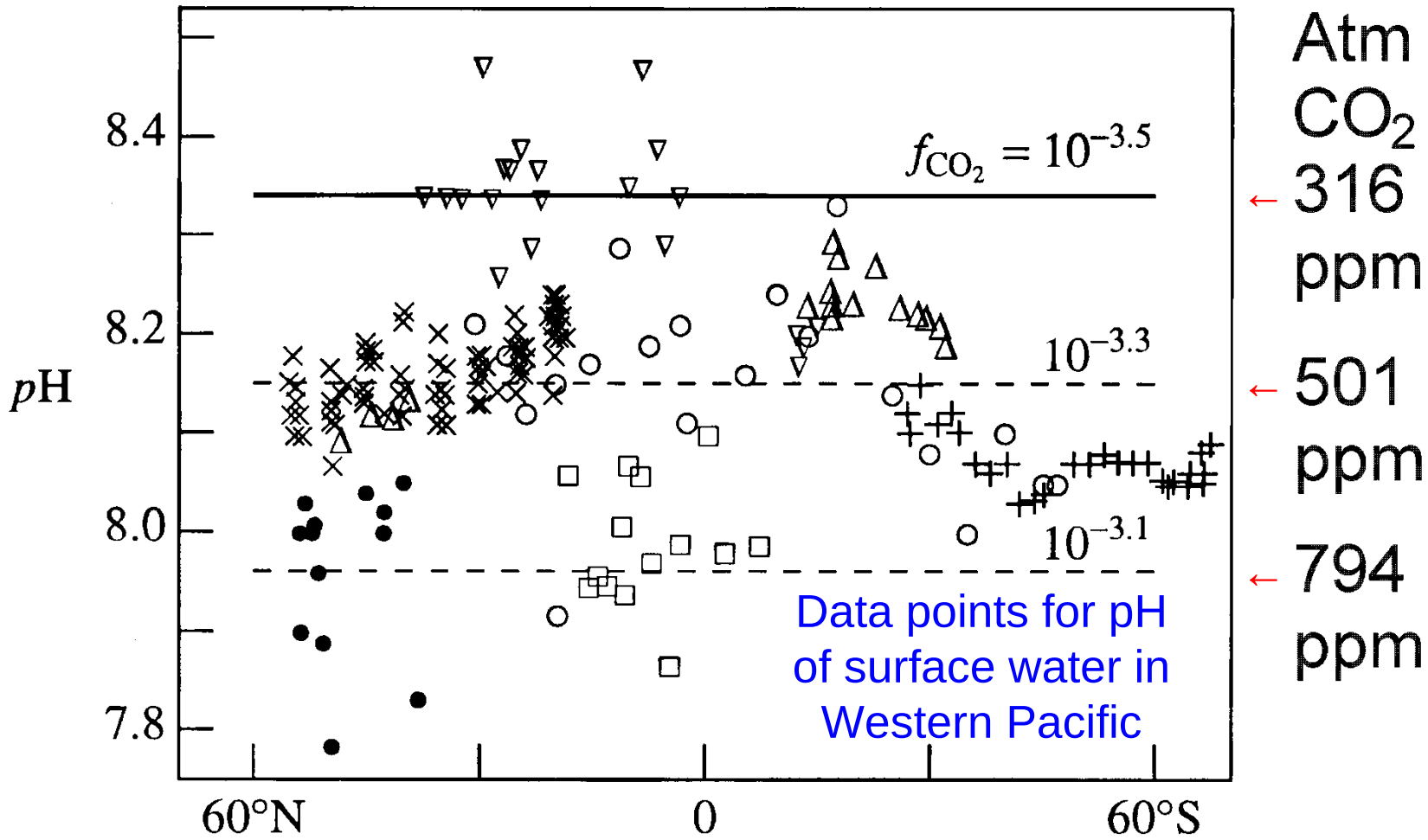
This means that there will be about 50 times more CO_2 dissolved in water than contained in the free air above.

The soda bottle is a good analogue to nature: there is about 50 times more CO_2 in the ocean than in the Earth's atmosphere.

Ocean water has 120mg HCO_3^- per liter; as much CO_2 as in 180 liter of air.

Acidification of the ocean?

- anomalies are within natural variation



Bethke (1996): Computed pH lines for ocean water with diff. CO_2 in air, **WITHOUT** minerals present

Buffers

A buffer can be defined as a reaction system which modifies or controls the value of an **intensive** (= mass independent) thermodynamic variable: Pressure, temperature, concentration, pH (acidity), etc.

CO_2 (g) + H_2O + Ca^{2+} (aq) ↔ $CaCO_3$ (s) + 2 H^+

The ocean's carbonate system will act as a pH buffer (pH = -log concentration of H^+) by the presence of a weak acid (H_2CO_3 and its protolysis derivatives) and a salt of the acid ($CaCO_3$).

The pH can be calculated as:

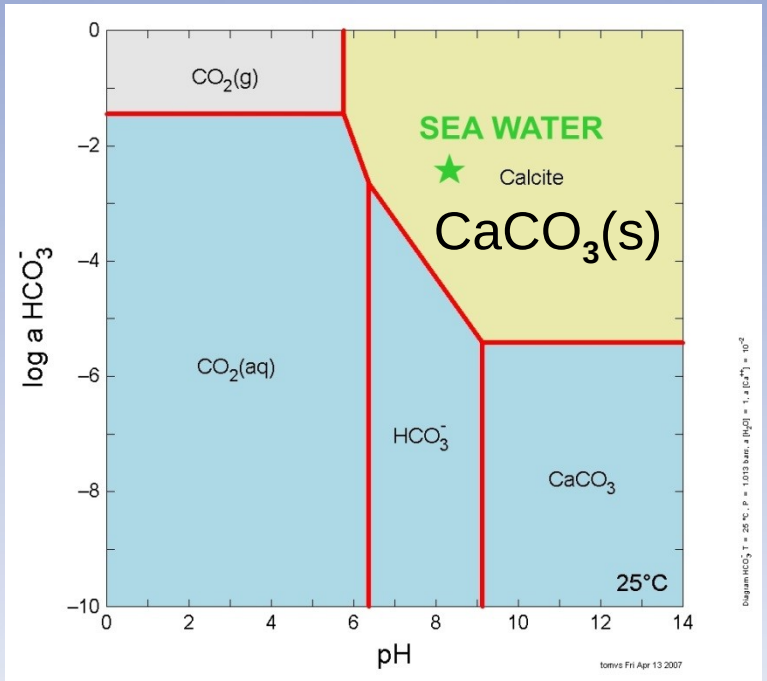
$$pH \approx [\log K + \log a(CO_2,g) + \log a(Ca^{2+},aq)] / -2$$

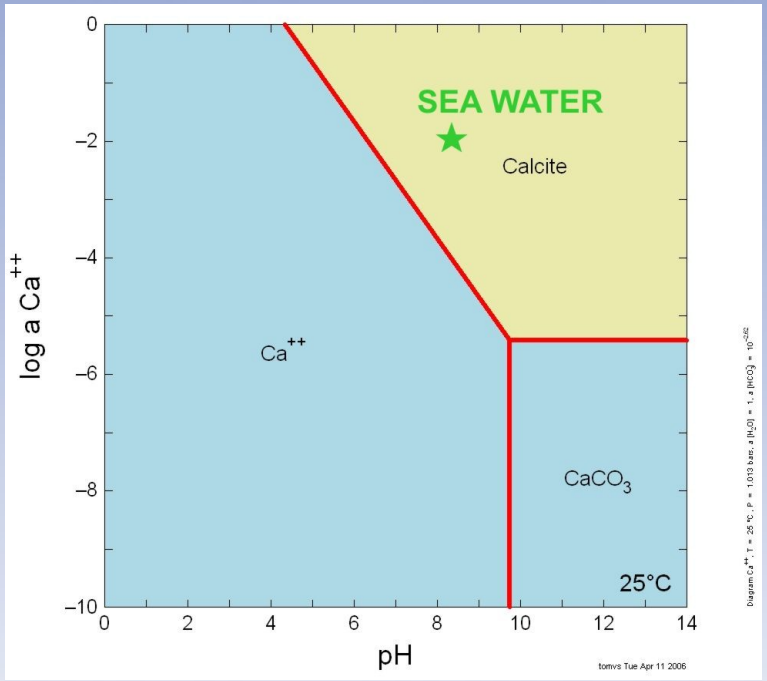
where K is the chemical equilibrium constant and a is the activity (thermodynamic concentration).

At the sea surface the $a(Ca^{2+},aq) >> a(CO_2,g)$.

If CO_2 had remained in the air => just small effect on pH.

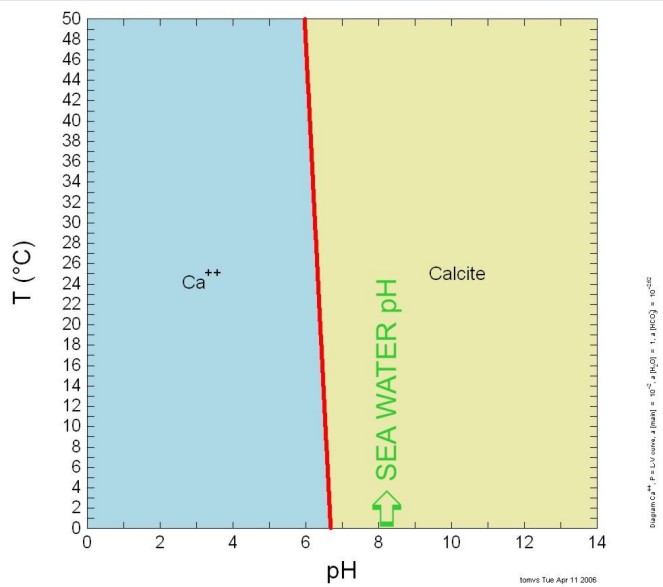
Ocean carbonate system





Increasing the amount of CO_2(g) alone will not dissolve $CaCO_3$ (s). pH must be decreased by 2 log units (100x H^+ concentration) in order to dissolve $CaCO_3$ at 25°C.

At 0°C the pH must be decreased by 1.5 units.



More ocean buffers

The carbonate buffer is not the only global buffer.
The Earth has a set of other buffering mineral reactions.

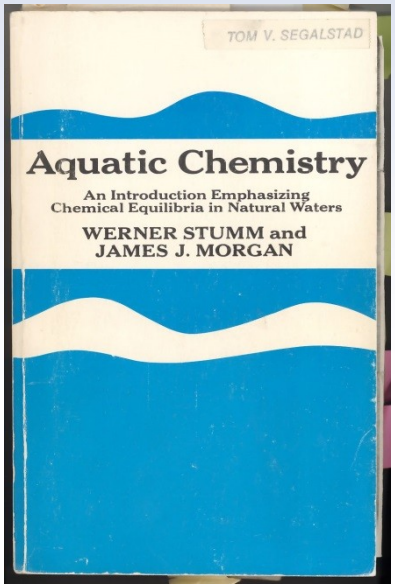
$$CaAl_2Si_2O_8\ (s) + 2H^+ + H_2O \leftrightarrow Al_2Si_2O_5(OH)_4\ (s) + Ca^{2+}\ (aq)$$

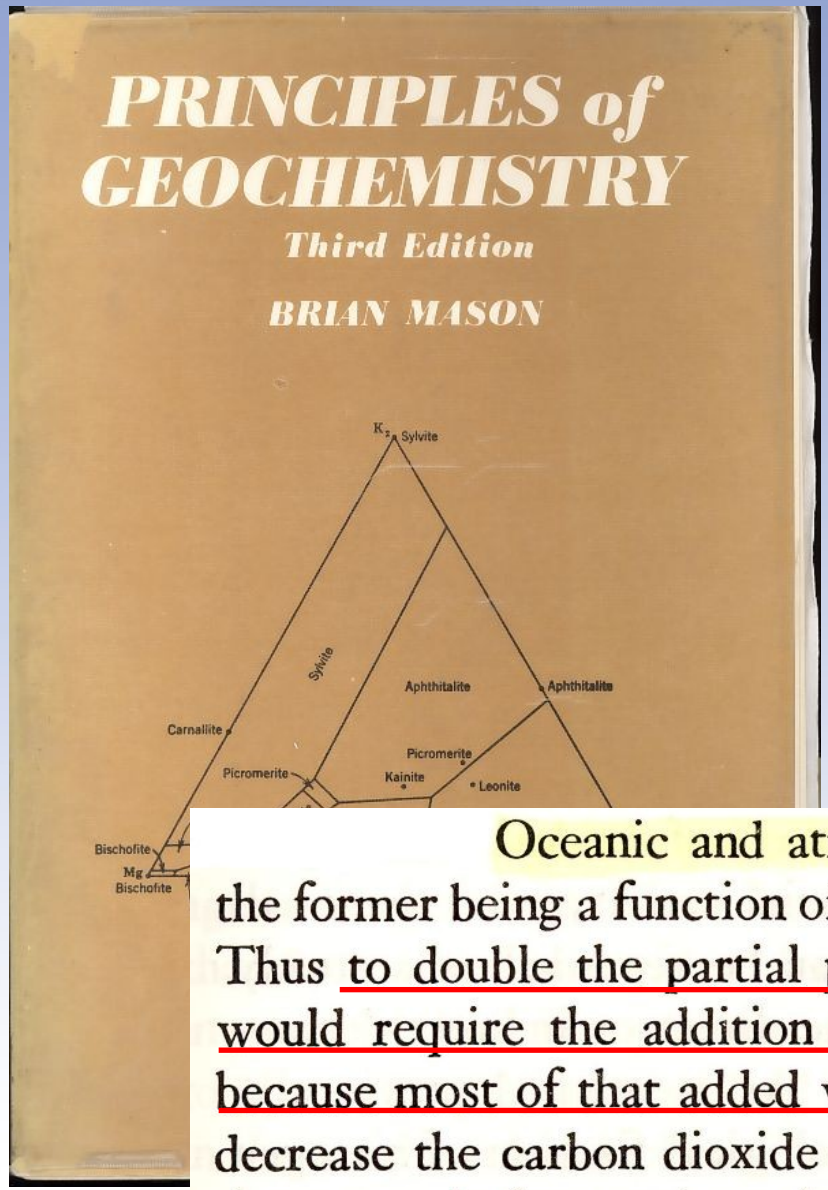
This anorthite feldspar ↔ kaolinite buffer has a buffer capacity *1000 times larger than the ocean's carbonate buffer*.

In addition we have clay mineral buffers *plus* a calcium silicate ↔ calcium carbonate CO_2-buffer [for simplicity]:

$$CaSiO_3 + CO_2 \leftrightarrow CaCO_3 + SiO_2$$

All these buffers will act as a ***"security net"*** under the CO_2 (g) ↔ $CaCO_3$ (s) buffer.
Together these add up to almost an ***"infinite buffer capacity"*** (Stumm & Morgan, 1970).





Brian Mason citations

"The ocean may thereby act as a self-balancing mechanism in which most of the elements have reached an equilibrium concentration."

We see this through a considerable constancy of sedimentation over the last hundreds of million years.

Oceanic and atmospheric carbon dioxide are interdependent, the former being a function of the partial pressure of CO_2 in the atmosphere. Thus to double the partial pressure of carbon dioxide in the atmosphere would require the addition of much more than is now present therein, because most of that added would be absorbed by the ocean; similarly, to decrease the carbon dioxide in the atmosphere by one half would require the removal of many times the present content. It is apparent that the oceans, by controlling the amount of atmospheric CO_2, play a vital part in maintaining stable conditions suitable for organic life on the earth.

But – *spectacular* facts are hard to beat…

"The picture's pretty bleak, gentlemen... The world's climates are changing, the mammals are taking over, and we all have a brain about the size of a walnut."