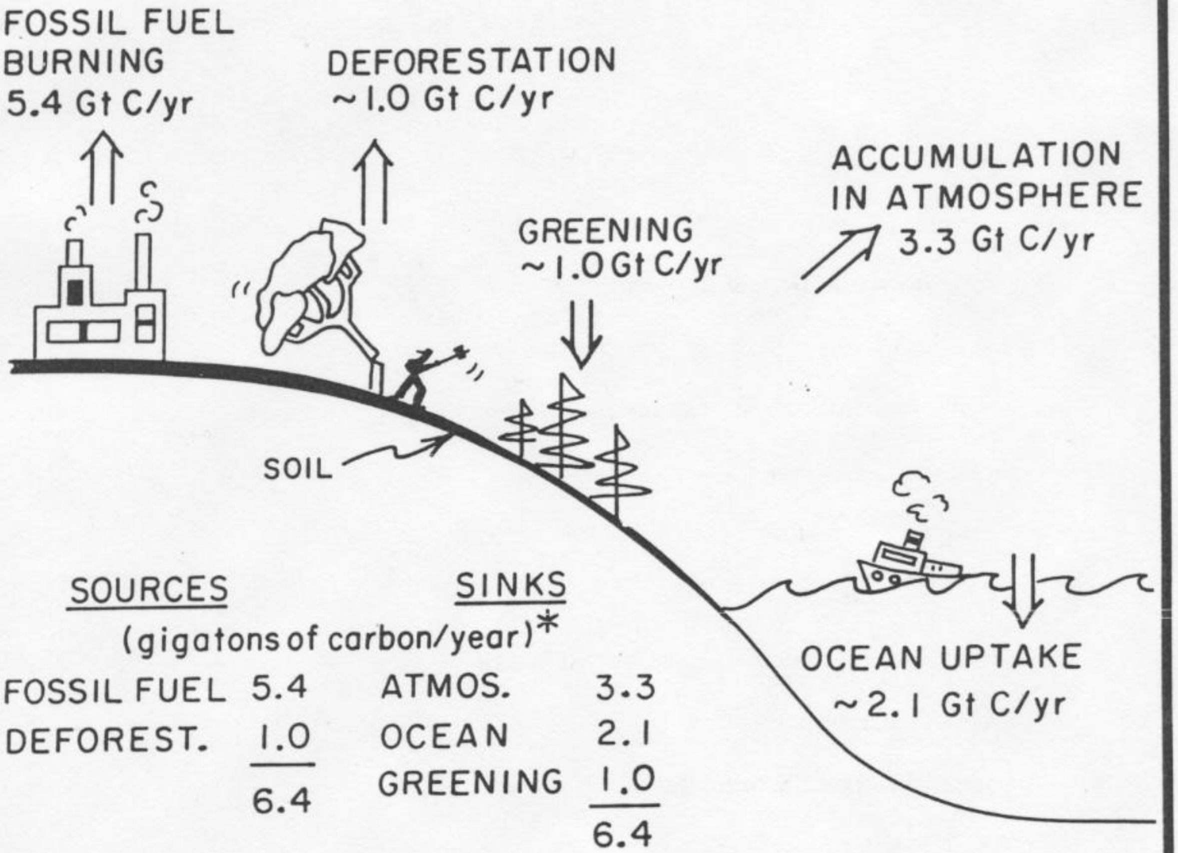
KEELING'S WORLD:

IS CO_2 GREENING THE EARTH?

This section's hero is Charles David Keeling. In the late 1950's, he had the wisdom to establish two stations for the continuous precise measurement of atmospheric carbon dioxide, one high on Hawaii's extinct volcano Mauna Loa and the other at the South Pole. The records from these stations provide the foundation upon which all studies of man's perturbation of the Earth's carbon cycle rest. Not only did Keeling have the foresight to establish these stations but also the tenacity to make sure that year in and year out they produced accurate results. Keeling took on this task as part of a career-long effort to understand the flux of CO_2 *gas through the atmosphere, into the ocean and into and out of the terrestrial biosphere. He was the first to realize the wealth of information contained in the spatial and seasonal texture of the atmosphere's* CO_2 *content. In addition to his direct scientific contribution, he fostered a secondary one. Son, Ralph, is doing for atmospheric* O_2 *all the kinds of things papa did for atmospheric* CO_2*.*

We know from the CO_2 content of air trapped in glacial ice that during the centuries prior to the Industrial Revolution, the CO_2 content of the Earth's atmosphere remained nearly constant. In other words, the world's carbon cycle remained close to steady state; removal of CO_2 through photosynthesis balanced its addition through respiration. But starting in the last century, activities of the expanding human population tipped the balance in favor of respiration. In response to the ever increasing demand for agricultural products, forests were cut and lands were tilled. These activities accelerated the oxidation of carbon stored in trees and in soil. In response to the expanding need for energy, engines fueled by coal, oil and natural gas proliferated. Organic matter which had survived for many tens of millions of years was recovered and burned. As a result of these activities, the CO_2 content of the atmosphere began a rise which steepened with each passing year. When this book was last revised, the CO_2 concentration was 30% higher than that for pre-industrial times

APROXIMATE EARTH CARBON BUDGET FOR THE 1980s; THE ANTHROPOGENIC PERTURBATION



(gigatons of carbon/year)*

SOURCES		SINKS	
FOSSIL FUEL	5.4	ATMOS.	3.3
DEFOREST.	1.0	OCEAN	2.1
	6.4	GREENING	1.0
			6.4

FRAC. TO ATMOS. $\frac{3.3}{6.4} = .52$

FRAC. TO SEA $\frac{2.1}{6.4} = .33$

FRAC. TO CONT. $\frac{1.0}{6.4} = .15$

$\overline{1.00}$

*1 Gt = 1×10^{15} grams
= 1×10^{9} tons

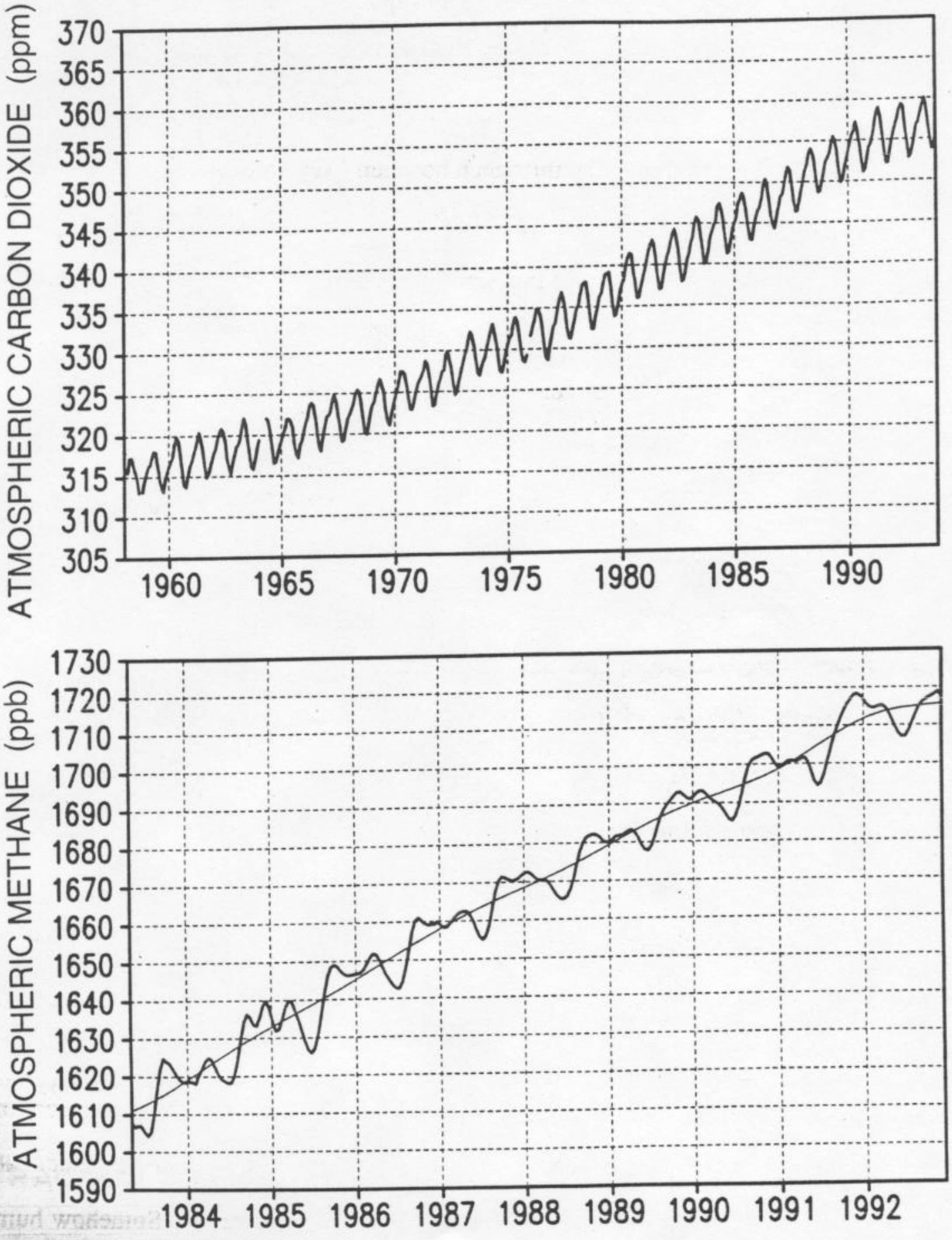
(in the year 1800, the CO_2 content was 280 parts per million ppm; as of 1997, it was 360 ppm).

This section's mystery is not that the atmosphere's CO_2 burden is rising, but rather that it is rising much more slowly than expected. The amount of excess CO_2 appearing in the atmosphere each year is just over one half that produced by fossil fuel burning. Nearly fifty percent has disappeared! The mismatch between CO_2 production and CO_2 buildup becomes even larger when the amount of CO_2 released as the result of forestry is taken into account. Although the magnitude of this activity remains poorly documented, during the last decade or so, an amount of CO_2 averaging about 25% that from coal, oil, and natural gas was released as the result of forest cutting. When this biosphere-derived CO_2 is included as a source term, the fraction of the CO_2 which remains airborne drops to only about 40% of the input. Where has the rest gone?

The most obvious hiding place is the ocean. Excess CO_2 in the atmosphere passes across the air-water interface and reacts with $CO_3^=$ ions dissolved in the sea to produce HCO_3^- ions. Were the atmosphere to be at chemical equilibrium with the entire ocean, about five sixths of the excess CO_2 would take up residence in the sea. Only one sixth would remain airborne. But it's not so simple; the sea mixes so slowly that only a small fraction of its capacity for CO_2 uptake is being utilized. Vast parts of the deep sea are accessible only on the time scale of hundreds of years. When this dynamic limitation is taken into account, it turns out that while the sea is an important hiding place, its uptake can account for only about one half the missing CO_2. Our mystery has to do with the fate of the remainder. Where has it gone?

The search for the so called "missing carbon sink" has been pursued for more than two decades. The conclusion is always the same. Only one reservoir, the organic matter which makes up the terrestrial biosphere, is big enough for the task. Somehow human activity must have increased the rate of photosynthesis. As a consequence, more carbon is being stored in tree trunks and soil humus. One might say, while the terrestrial biosphere

ANTHROPOGENIC INCREASES IN ATMOSPHERIC CO_2 AND CH_4

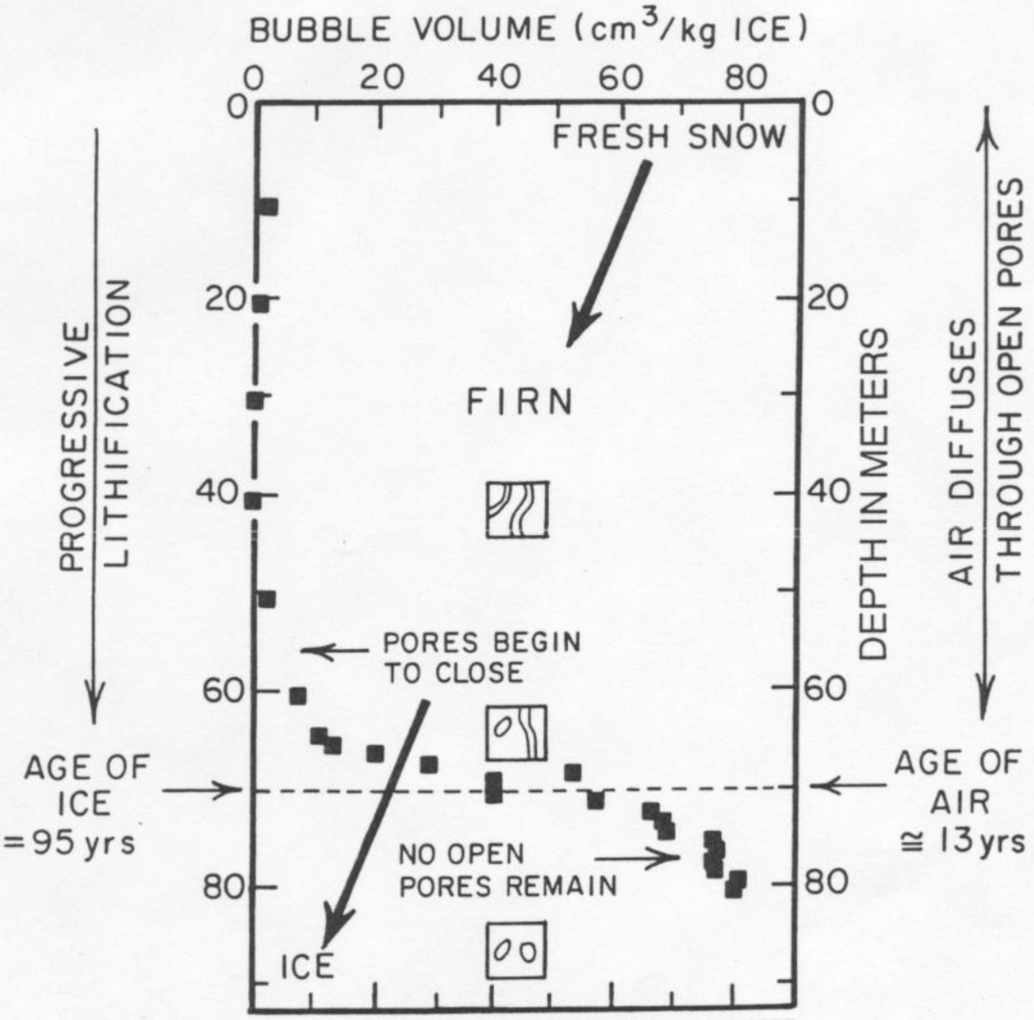


reservoirs is being trimmed around the edges, it is becoming more lush in the interior. Through our activities, we have been "greening", not just agricultural land but the entire planet. Actually, agricultural land is part of the problem, and not of the solution. First, as plants grown on agricultural land are harvested each year, no above ground storage of carbon occurs. More important, agricultural practice has been shown to drive down the humus content of soil. So, if the missing carbon is being packed away in wood and humus, this storage is occurring on lands we classify as uncultivated.

Two mechanisms have been identified which might propel a global greening. The first involves CO_2 itself. As carbon is the primary building block for plant matter, the increased abundance of CO_2 in the atmosphere might be expected to accelerate photosynthesis. More CO_2 flows into the factory allowing more organic matter to be manufactured. Indeed, experiments carried out in growth chambers suggest that, at least on the short term, a 30% increase in the CO_2 content of the air leads to growth enhancements averaging 10%. If CO_2 is driving an enhancement of this magnitude in the wild, then, each year more wood is being generated (leading to fatter forests) and more organics are being pumped into soils (leading to richer humus). The second mechanism involves nitrogen. Growth in most plant communities is often limited by the availability of this important nutrient. Farmers counter this deficiency by fertilizing their fields with ammonia or by allowing them to remain fallow so that plants with nitrogen-fixing root symbionts can generate natural fertilizer. The internal combustion engine extends nitrogen fertilization to the wilds. Atmospheric N_2 molecules are split at the high temperatures achieved in automobile engines producing nitrogen oxide gases. These gases become widely dispersed through the atmosphere before they are transformed to nitric acid molecules which dissolve in raindrops. This automobile-generated fertilizer allows more wood and soil humus to be generated. While a strong case can be made that extra carbon dioxide and fixed nitrogen are greening the planet, as we shall see, this greening process must be operating at maximum efficiency if it is to account for the storage of the missing

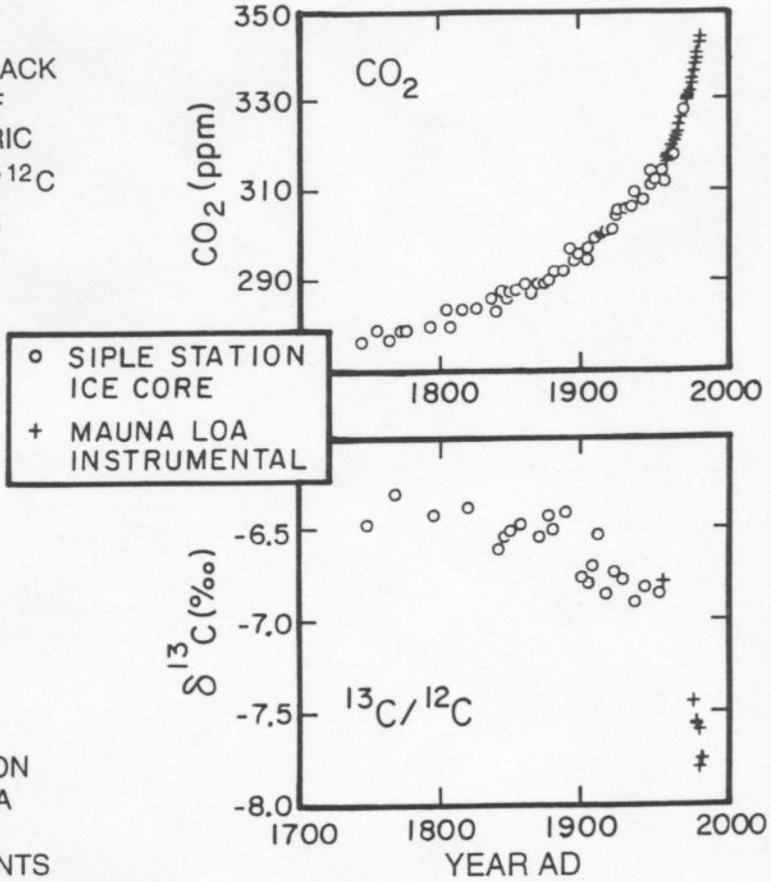
RELATIONSHIP BETWEEN AGE OF ICE AND AGE OF AIR TRAPPED IN BUBBLES IN ICE FOR SIPLE STATION ANTARCTICA

$T_{AIR} = T_{ICE} - 82$ YEARS



SCHWANDER & STAUFFER
BERN, SWITZERLAND

EXTENSION BACK
IN TIME OF
ATMOSPHERIC
CO_2 AND $^{13}C/^{12}C$
RECORDS



SIPLE STATION
ANTARCTICA
ICE CORE
MEASUREMENTS

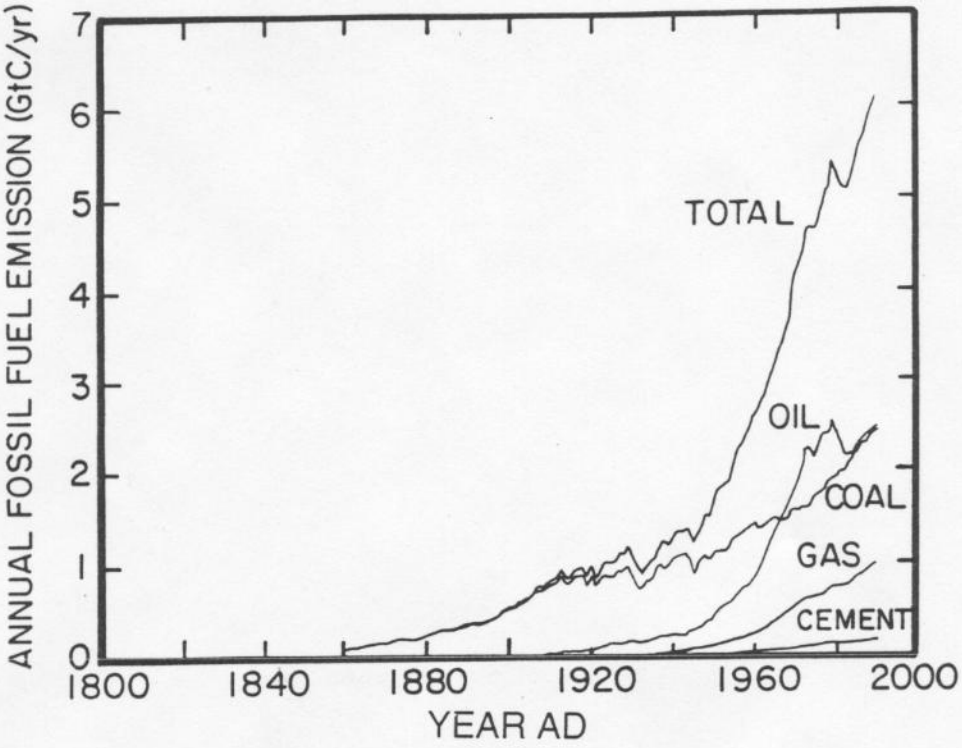
Depth (m)	Ice Age (yr. AD)	Gas Age (yr. AD)	CO_2 (ppm)	$\delta^{13}C$ (‰)
81.22	1871	1953	312.7	- 6.85
86.80	1861	1943	307.9	- 6.82
90.77	1853	1935	306.6	- 6.91
95.17	1845	1927	305.5	- 6.78
98.80	1839	1921	301.6	- 6.74
101.80	1833	1915	300.5	- 6.86
105.25	1827	1909	299.2	- 6.54
107.20	1823	1905	296.9	- 6.71
108.80	1821	1903	294.8	- 6.80
110.20	1817	1899	295.8	- 6.77
116.82	1805	1887	292.3	- 6.42
121.80	1796	1878	290.3	- 6.51
123.80	1792	1874	289.5	- 6.43
126.80	1787	1869	289.3	- 6.55
134.47	1772	1854	288.2	- 6.48
138.20	1765	1847	286.8	- 6.51
140.75	1761	1843	287.4	- 6.54
142.75	1757	1839	283.1	- 6.62
154.89	1734	1816	283.8	- 6.39
168.30	1709	1791	279.7	- 6.43
177.50	1682	1764	276.7	- 6.31
187.70	1662	1744	276.8	- 6.48

← ANNUAL LAYER 113

← ANNUAL LAYER 322

FRIEDLI AND COWORKERS, BERN, SWITZERLAND

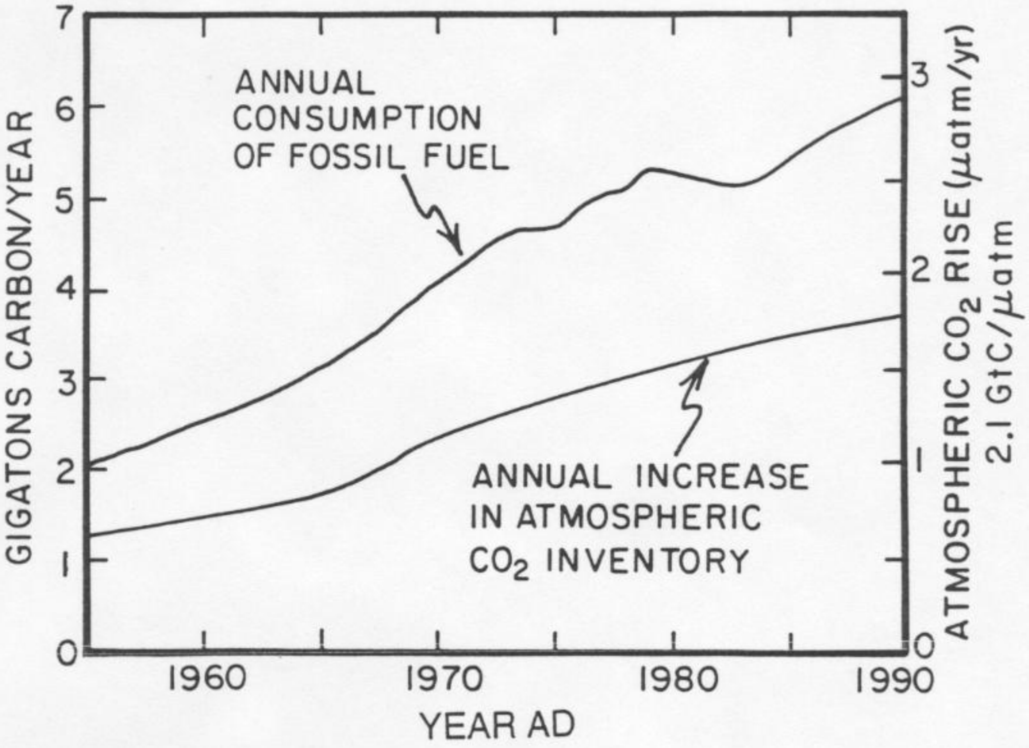
TIME HISTORY OF FOSSIL FUEL CONSUMPTION



FOSSIL FUEL EMISSIONS (GtC/yr)

	1950	1960	1970	1980	1990
COAL	1.1	1.4	1.6	2.5	2.5
OIL	0.4	0.9	1.8	1.9	2.4
GAS	0.1	0.2	0.5	0.7	1.0
$CaCO_3$	0.0	0.0	0.1	0.1	0.2
TOTAL	1.6	2.5	4.0	5.2	6.1

COMPARISON WITH THE RATE OF ACCUMULATION OF CO_2 IN THE ATMOSPHERE



OVER THE TIME PERIOD DURING WHICH THE ATMOSPHERE HAS BEEN ACCURATELY MONITORED, ITS CO_2 CONTENT HAS BEEN RISING AT A RATE ONLY ABOUT 60% THE RATE EXPECTED IF ALL THE FOSSIL FUEL CO_2 RELEASED REMAINED AIRBORNE.

carbon. Before exploring this question, let us review the evidence upon which carbon budgets are based.

The Knowns

Only two of the terms in the carbon budget are directly measured to a reasonably high degree of accuracy. One is the amount of CO_2 generated during each of the last 100 or so years through the burning of fossil fuels and the manufacture of cement. The number of tons of coal mined, the number of barrels of oil pumped, the number of cubic meters of natural gas recovered, and the number of tons of limestone thermally decomposed have been laboriously compiled from records kept by individual nations. The other is the CO_2 content of the atmosphere. In 1957, Charles David Keeling commenced continuous highly accurate measurement of the CO_2 content of air atop the extinct volcano Mauna Loa on the island of Hawaii. Keeling's measurement series has continued unbroken and is now supplemented by measurements at many other locations on our planet. Scientists at Bern, Switzerland and Grenoble, France discovered a means of extending this record back in time. Their trick was to extract gas stored in the bubbles contained in ice recovered from borings atop the Greenland and Antarctic ice caps. They demonstrated that this mode of cold storage nicely preserves the CO_2 content of the trapped air.

These two sets of data constitute our givens. Taken together, they tell us with clarity that, over the time spanned by the instrumental record, CO_2 has built up in the atmosphere at a bit more than one half the rate it was being generated by fossil fuel burning. The remaining three budgetary terms (described in the sections which follow: ocean uptake, deforestation, and greening) must be estimated by less direct means.

The Mirror Image Approach

The CO_2 produced by the burning of fossil fuels must be matched by an equivalent consumption of atmospheric oxygen. For coal, about thirteen molecules of O_2 disappears for each ten atoms of carbon combusted.

$$C_{10}H_6 + 13O_2 \rightarrow 10CO_2 + 3H_2O$$

For petroleum, the ratio is close to 3 O_2 molecules for each 2 carbon atoms.

$$2CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

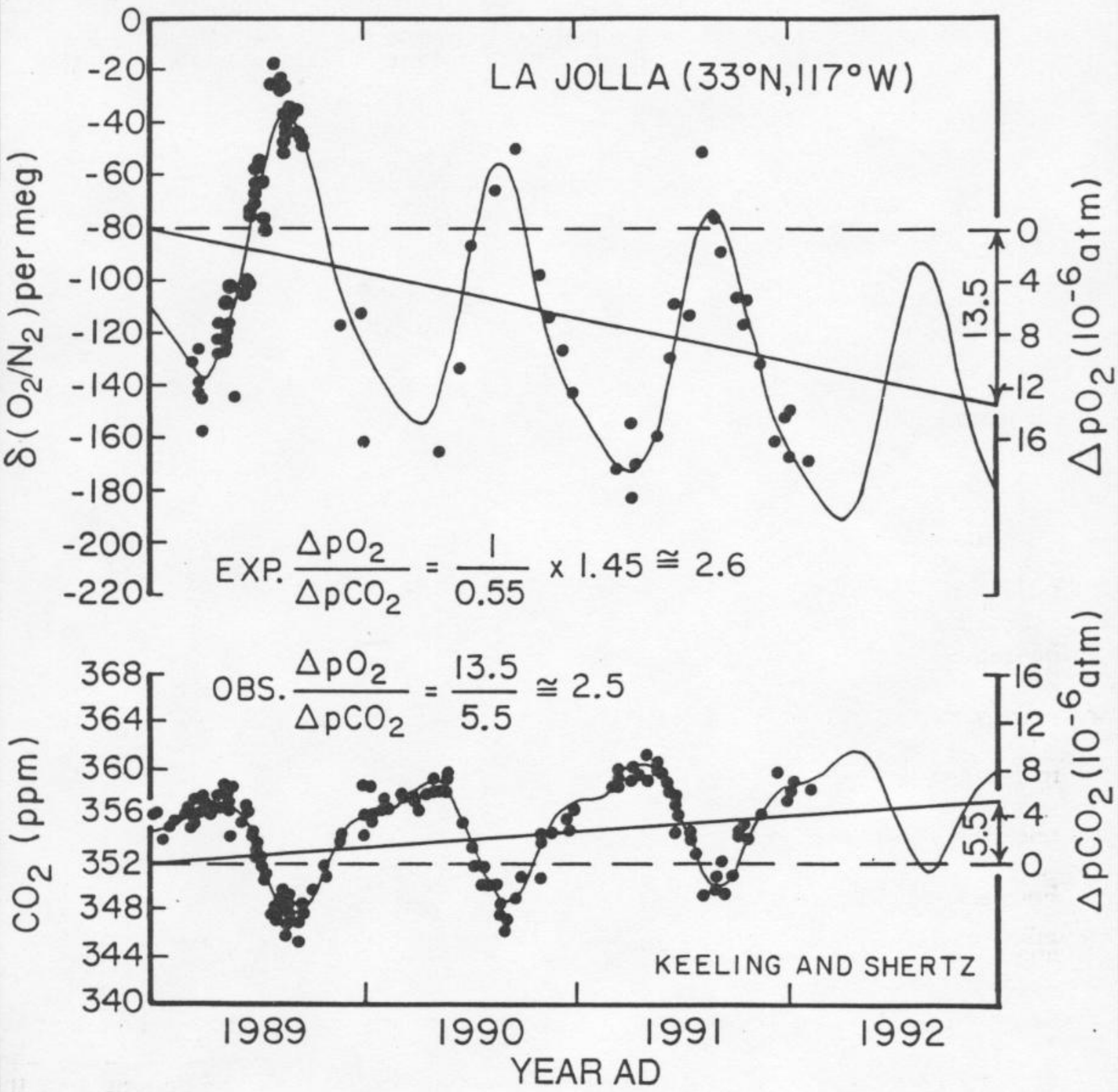
For natural gas, the ratio is 2 to 1.

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

The current global mix of these three fuels requires the consumption of 15 molecules of O_2 for each 10 molecules of CO_2 produced. The mirror image strategy is a simple one. The measured rate of O_2 decline is compared with that expected from the amount of fossil fuels consumed. One might ask what advantage this information would have over that obtained from comparing the observed rate of rise in atmospheric CO_2 content with the expected rate. There is a very important difference. While the ocean is capable of absorbing five sixths of all the CO_2 we have produced (and thereby constitutes a very important term in the carbon budget), no comparable term exists in the O_2 budget. The reason is that 95 percent of the earth's O_2 resides in the atmosphere and only 5 percent in the ocean. The tiny amount of O_2 which will flow from the ocean back to the atmosphere to compensate for the loss through fossil fuel burning is unimportant in the O_2 budget. Thus O_2 budgeting is far simpler than CO_2 budgeting. Dead simple in fact. The difference between the observed rate of O_2 disappearance and that expected from fossil fuel burning provides a measure of the rate of change in the overall global biomass. For each molecule of CO_2 released to the atmosphere through deforestation, about one molecule of O_2 disappears. For each unit atom of carbon stored in wood or humus as the result of global greening, about one molecule of O_2 will be released to the atmosphere. Thus if more O_2 is disappearing than required for fossil fuel combustion, then the biosphere as a whole must be shrinking. Or if less O_2 is disappearing than required for fossil fuel burning, then the biosphere must be expanding.

But two difficulties remain. As already discussed, the biospheric carbon inventory is being influenced in opposing ways by man. Farmers and foresters are reducing its size. Greening by excess CO_2 and fixed nitrogen is increasing its size. So, for example, were

COMPARISON BETWEEN ATMOSPHERIC CO_2 AND O_2 RECORDS

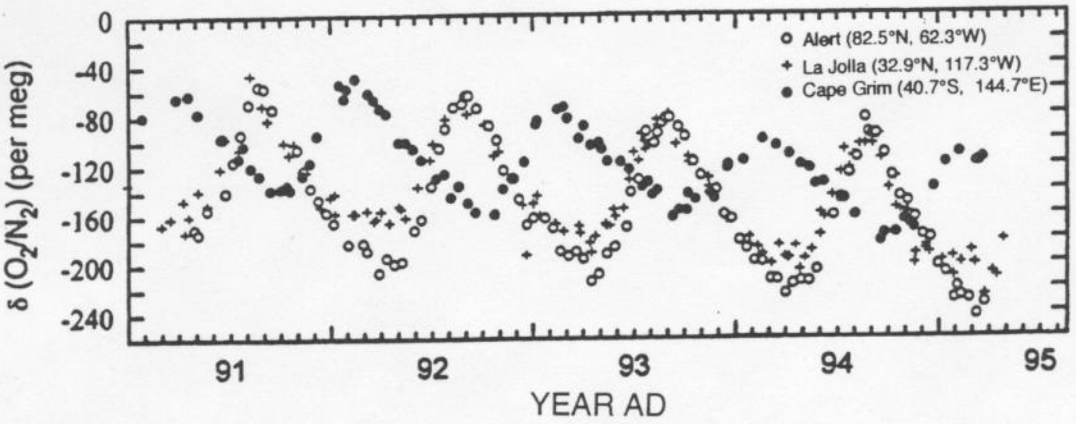


measurements to reveal that O_2 is declining exactly in accord with expectation from fossil fuel burning, it would mean that losses driven by forestry and agriculture were, by chance, just balanced by gains driven by greening. In order to reach our goal of establishing how much greening is occurring, it is necessary to quantify reduction in wood and humus stocks.

The second obstacle is one of measurement. In 1997, the atmosphere contained 364 ppm CO_2. Two years from now, it will contain 367 ppm. This increase can be documented precisely with modern instrumentation. By contrast, the atmosphere contains about 209,000 ppm of O_2. The expected drop during the same two-year period from fossil fuel burning alone is about 5 ppm. This represents a change of only 0.0025%; a daunting challenge to even the most clever experimentalist.

The second challenge was not met until 1989 when Ralph Keeling succeeded in developing a method capable of determining changes in the O_2 content in air to an accuracy of 0.8 ppm. Then, working together with his colleague Shertz, he succeeded in demonstrating that over the three-year period from 1989 to 1992, the O_2 content of air in La Jolla, California dropped at a rate consistent with that expected from global fossil fuel burning. However, at that point the uncertainty in this result was big enough to permit the possibility that the biosphere was either shrinking or expanding at a rate up to 2 gigatons a year. As this range covers virtually all possible scenarios, this early measurement series didn't help much. But as the years clicked by, Keeling's O_2 measurements began to pay off. In fact, he has been able to document an amazing occurrence. Between 1989 when his measurement series began and 1995, the O_2 content of the atmosphere dropped considerably less than would be expected. Taken together with the rise in CO_2 over this period, this shortfall in the magnitude of the O_2 decline indicates that during this period the split of fossil fuel CO_2 flow was 35% to atmosphere, 35% to the ocean, and 30% to the biosphere. This came as a big surprise indicating that the biosphere was taking up an average of about two gigatons of carbon per year during this time interval. If, for example,

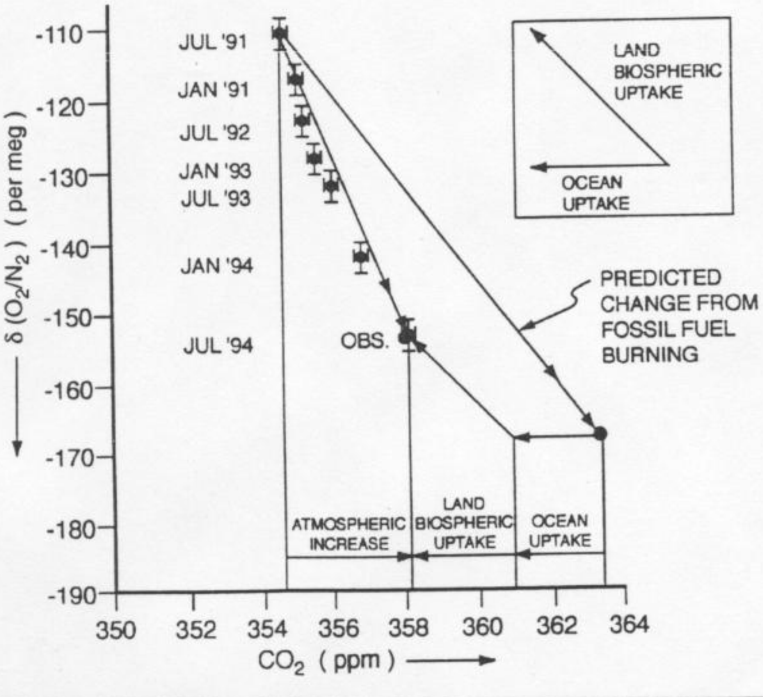
O_2 - CO_2 SYSTEMATICS



$$\delta \frac{O_2}{N_2} = \left(\frac{O_2/N_{2\ \mathrm{SAMP}}}{O_2/N_{2\ \mathrm{STD}}} - 1 \right) \times 10^6$$

4.8 per meg = 1 μatm O_2

PO_2 = 209,500 μatm



forest cutting was releasing one gigaton of carbon per year, this would require a greening of roughly three gigatons a year! We will return to this finding later in this section, but before going on, it must be stated that this rate of greening need not be entirely or even largely anthropogenic. Rather, it might reflect unusually favorable growth conditions across the globe. Even though averaged over many years, respiration must match growth; a pulse in global photosynthesis over a several year period could temporarily outstrip respiration. It is likely that such a pulse occurred in the early 1990s. If so, then respiration will soon gain the upper hand and eliminate this short term excess storage. This finding emphasizes the need for a record of sufficient duration so that the influence of changes in global photosynthesis induced by short term climate changes can be averaged out.

Shortly after Keeling developed his index of refraction technique for precise O_2/N_2 ratio measurement, Sowers and Bender came up with a nearly as precise a means to accomplish this task using conventional mass spectrometry. Impatient with the prospect of the long wait for a definitive result, they developed a hindcasting method. It involves getting air samples from deep in the 70 or so meter thick layer of firn which caps the Antarctic and Greenland ice caps. Firn is partially lithified snow which has open pores which provide access to the overlying atmosphere. But diffusion of gases through this matrix is so slow that the gas deep in the firn is replaced only once per decade or so. The first measurements by Sowers and Bender showed that indeed air from deep in the firn had a higher O_2/N_2 ratio than that in the atmosphere. It also had lower methane and carbon dioxide contents. As the evolution of the methane and carbon dioxide contents of the atmosphere over the last decade or so are well documented, these measurements served to fix the average age for any given sample of firn air. Based on this age and the O_2/N_2 ratio, Sowers and Bender hoped to obtain a rate of O_2 decline for decades past. But again the uncertainty in these preliminary measurements is too great to provide a definitive answer. The reason is that despite the 5 times greater length of the Sowers-Bender record, the measurement uncertainty is considerably larger. While firn provides a superb storage environment in that it is very cold, very dry, free of bacteria, and immune to contamination from underlying earth gas, it is not perfect. The long residence time of gas in the firn allows preferential settling of heavy molecules relative to light ones. As O_2 (mass 32) is heavier than N_2 (mass 28), this settling alters the ratio of interest. Sowers and Bender were, however, armed with a means to correct for this gravitational settling effect. They measured the ratio of $^{15}N^{14}N$ (mass 29) to $^{14}N^{14}N$ (mass 28) in the same samples and used the enrichment of the heavy nitrogen molecule as a basis to correct for the gravitational enrichment of O_2 relative to N_2.

As the record in firn extends back only 10 to 20 years, in order to be successful the Sowers and Bender approach will have to be extended beyond the base of the firn into the underlying ice. In attempting this extension, they have encountered a serious problem. As the bubbles of trapped gas closed off, air diffuses in and out of the tiny residual orifices creating a small separation between O_2 and N_2. In an attempt to develop a means to correct for this separation, Jeff Severinghaus and Michael Bender are currently measuring the Ar to N_2 ratios as well as the O_2 to N_2 ratios in firn and ice. So the question is whether the hares (Bender and coworkers) springing rapidly back time can put aside potential biases created by ice storage and beat out the tortoises (Keeling and coworkers) who are forced to plod along one year at a time. Clearly, however, both results are of extreme importance. One will give information about the state of the biosphere during the coming decades, and the other about its state during past decades.

Ocean Uptake

Another way to approach carbon budgeting is to estimate without the use of O_2 data the uptake of CO_2 by the ocean. Once this term has been defined, then change in the Earth's biomass can be calculated by subtracting the CO_2 increases in the ocean and atmosphere reservoirs from the total amount of CO_2 produced by man's activities. The first point to be made in this regard is that ocean uptake cannot, at present, be estimated from the results of repeated ΣCO_2 inventories. Unlike the atmosphere for which a combination of measurements on air bubbles stored in ice (prior to 1958) and direct sampling (after 1958) provide a complete record of the inventory's evolution, we have no equivalent for the ocean. The first detailed and accurate global survey of the dissolved inorganic carbon content of ocean water (ΣCO_2) was made during the 1970s as part of the GEOSECS (Geochemical Ocean Sections Study) expeditions. But even these measurements were not of sufficient accuracy to provide an adequate base for future surveys. The problem is that even for waters which have taken up their full component of excess CO_2, the increase in ΣCO_2 since the 1970s has only been about one percent. The accuracy of the GEOSECS measurements is no better than 0.5%. Of course, the situation is even less favorable for sub-surface waters which have achieved only a fraction of their uptake capacity. Because of this, the direct inventory approach is at present hopeless.

During the 1990's, a far more detailed and accurate (to ±0.1%) survey was made under the banner of the global WOCE (World Ocean Circulation Experiment) program. If a similar survey is conducted 15 to 25 years hence, it will then be possible for the first time to directly measure the integrated CO_2 uptake by the ocean. But of course this result will apply only to the time between the two surveys.

In the interim, the amount of excess CO_2 which has entered the ocean must be obtained by less direct means. One approach involves ocean models designed to take into account not only the thermodynamic capacity of sea water for the uptake of excess CO_2 but also the two kinetic barriers to its uptake, namely, the resistance posed by transport across the air-sea interface and the resistance posed by vertical mixing within the sea. These models are initialized so as to be at steady state with the pre-industrial atmosphere (pCO_2 =280 µatm). Then the model's atmospheric CO_2 content is time stepped to follow the observations. After each step, CO_2 is exchanged between the atmosphere and surface ocean and mixing occurs within the ocean. The output of the model is the evolution of the storage of excess CO_2 in the ocean.

THERMODYNAMIC CAPACITY FOR CO_2 UPTAKE

IDEALIZED SEA WATER (NO BORATE)

CHARGE BALANCE

$$[Na^+]+[K^+]+2[Mg^{++}]+2[Ca^{++}]=[Cl^-]+2[SO_4^=]+[HCO_3^-]+2[CO_3^=]$$

OR

$$[Na^+]+[K^+]+2[Mg^{++}]+2[Ca^{++}]-[Cl^-]-2[SO_4^=]=[HCO_3^-]+2[CO_3^=]$$

OR

$$[ALKALINITY]=[HCO_3^-]+2[CO_3^=]$$

MASS BALANCE FOR DISSOLVED INORGANIC CARBON

$$[\Sigma CO_2]=[CO_2]+[HCO_3^-]+[CO_3^=]$$

CHEMICAL EQUILIBRIUM

$$CO_2+CO_3^=+H_2O \Longleftrightarrow 2HCO_3^-$$

$$K_c' = \frac{[HCO_3^-]^2}{[CO_2][CO_3^=]} \quad , \quad \alpha = \frac{[CO_2]}{pCO_2} = 0.342\ \frac{\mu mol/kg}{\mu atm}$$

EXAMPLE T = 18°C S = 35‰ $K_c' = 1445$ ALK = 2100

$pCO_2 = 280\mu atm$	$pCO_2 = 360\mu atm$	Δ
$[CO_2]$ = 9.6	$[CO_2]$ = 12.3	+2.6 μmol/kg
$[HCO_3^-]$ = 1700	$[HCO_3^-]$ = 1769	+69 μmol/kg
$[CO_3^=]$ = 200	$[CO_3^=]$ = 166	−34 μmol/kg
$[ALK]$ = 2100	$[ALK]$ = 2100	0 μmol/kg
$[\Sigma CO_2]$ = 1910	$[\Sigma CO_2]$ = 1948	+38 μmol/kg

$$\text{REVELLE FACTOR} = \frac{\Delta pCO_2/pCO_2}{\Delta\Sigma CO_2/\Sigma CO_2} = \frac{80/280}{38/1910} = 14.4$$

ACTUAL SEA WATER (INCLUDING BORATE)

CHARGE BALANCE

$$[\text{ALKALINITY}] = [HCO_2^-] + 2[CO_3^=] + [H_4BO_4^-]$$

MASS BALANCE BORON

$$[\Sigma B] = [H_3BO_3^0] + [H_4BO_4^-] = 410.6\,\frac{S}{35}\,\mu\text{mol/kg}$$

CHEMICAL EQUILIBRIUM

$$K_B' = \frac{[H_4BO_4^-]\,[HCO_3^-]}{[H_3BO_3^0]\,[CO_3^=]}$$

EXAMPLE T = 18°C S = 35 ‰ $K_C' = 1482$ $K_B' = 2.75$
ALK = 2216 $SiO_2 = 0$ $NO_3 = 0$ $PO_4 = 0$

$pCO_2 = 280\,\mu atm$	$pCO_2 = 360\,\mu atm$	Δ
$[CO_2]$ = 9.6	$[CO_2]$ = 12.3	+2.6 µmol/kg
$[HCO_3^-]$ = 1702.5	$[HCO_3^-]$ = 1779.5	+77.0 µmol/kg
$[CO_3^=]$ = 203.7	$[CO_3^=]$ = 173.1	−30.6 µmol/kg
$[\Sigma CO_2]$ = 1915.8	$[\Sigma CO_2]$ = 1964.9	+49.1 µmol/kg
$[H_3BO_3^0]$ = 308.9	$[H_3BO_3^0]$ = 323.9	+15.0 µmol/kg
$[H_4BO_4^-]$ = 101.7	$[H_4BO_4^-]$ = 86.7	−15.0 µmol/kg
$[\Sigma B]$ = 410.6	$[\Sigma B]$ = 410.6	0.0 µmol/kg
$[OH^-]$ = 4.4	$[OH^-]$ = 3.6	−0.8 µmol/kg
$[ALK]$ = 2216.0	$[ALK]$ = 2216.0	0.0 µmol/kg

$$\text{REVELLE FACTOR} = \frac{\Delta pCO_2 / pCO_2}{\Delta\Sigma CO_2 / \Sigma CO_2} = \frac{80/280}{49.1/1915.8} = 11.1$$

Commentary on Keeling's World Plates

pg. 2

The concensus view of the annual perturbations experienced by various Earth surface carbon reservoirs during the 1980s. The fossil-fuel source is estimated from records of coal, oil and natural gas production kept by each nation. The deforestation contribution is estimated using satellite photography and ground-based standing biomass measurements. The magnitude of ocean uptake is based on modeling. Greening (i.e., the increase in terrestrial biomass resulting from CO_2 and fixed N-induced growth enhancement) is determined by difference.

pg. 4

In the upper panel is shown the atmospheric CO_2 record for Marina Loa Hawaii from 1958 to 1993. In addition to the temporal trend driven by fossil fuel burning, there are internal changes resulting from small mismatches between respiration and photosynthesis (see for example, the dramatic flattening in the early 1990s). The seasonal cycle is driven by the strong late spring and early summer drawdown of CO_2 by plant growth in the extensive northern hemisphere temperate regions. In the lower panel is shown the atmospheric methane record.

pgs. 6-7

Sufficiently accurate direct measurements of the CO_2 content of the atmosphere are available only for the period 1958 to present. Fortunately, this record can be extended back in time using air trapped in polar ice. One problem in this regard is establishing the exact age of the trapped air. Measurements on material from a shallow core from Antarctica show that the close off of pores in the firn begins at a depth of 60 meters and is complete by about 80 meters. The age of the siple ice at the depth of the midpoint of this close off interval is 95 years (as determined by counting annual layers). Based on CFC measurements, the replacement of the air at the base of the firn via diffusion down through the web of pores is estimated to be about 13 years. Hence the air in bubbles is 82 years less than that of the ice in which the bubbles are encased. Of course, as the bubble close off is not instantaneous but is spread over a period of time and as the diffusive ventilation of the firn mixes air of different ages, the air trapped at any given depth is a mixture spanning a decade or so.

As can be seen on page 7, the ice-core-derived reconstruction of atmospheric CO_2 content and of an $^{13}C^{12}C$ tie in nicely with atmospheric measurements.

pgs. 8-9

Breakdown of the magnitude of individual CO_2 sources as a function of time. While the dramatic use of petroleum use leveled off in the early 1970's, coal and natural gas took up the slack. Since 1957 when CO_2 monitoring began, the rate of increase of the atmosphere's CO_2 content has averaged about 60 percent the rate of CO_2 emissions from fossil fuel burning.

p. 12

Comparison of the La Jolla, California record for O_2 decline with that for the CO_2 rise. When the seasonal cycle is removed, O_2 shows a 13.5 µatm decline over this period and CO_2 a 5.5 µatm rise. Two reasons exist for this difference. First, 145 moles of O_2 are required to produce 100 moles of CO_2 (the extra oxygens are required to convert the H in the fuel to H_2O). Second, part of the CO_2 goes into the ocean.

pg. 14

In the upper panel is shown the relationship between atmospheric O_2 trend for a four-year period. In the lower panel is a comparison between the predicted and observed cumulative trends for O_2 and CO_2. The predicted trend is that expected if the atmosphere were a closed system. In order to account for the difference between the observed and predicted trends, it is necessary to invoke not only CO_2 uptake by the ocean but also a significant increase in the amount of carbon stored in the terrestrial biosphere.

pgs. 18-19

Sea water takes up significant amounts of fossil fuel CO_2 mainly because it is a basic solution. CO_2 from the atmosphere mates with carbonate ion in the sea to form two bicarbonate ions. As shown on the left, were sea water free of borate, the reaction carbonate ion would enhance the uptake by more than a factor of 13 (i.e., 34/2.6) over that resulting from the solution of CO_2 gas alone. When the reaction with borate is included, the enhancement of uptake reaches almost a factor of 19 (i.e., 49.1/2.6). Also note that by adding fossil fuel CO_2 to the sea, we are gradually eroding its capacity for further uptake. Both the $CO_3^=$ and $H_4BO_4^-$ are being consumed. The Revelle factor is the percentage increase in the partial pressure of CO_2 in the atmosphere required to raise the ΣCO_2 content of surface sea water by one percent.

pgs. 20-21

Radon measurements in the ocean-mixed layer provide an estimate of the rate at which gases pass back and forth across the air-sea interface. By measuring the ratio of radon concentration in the water to that which would be present were no radon to escape to the atmosphere (i.e., that amount of ^{222}Rn were its decay rate to just match its production by the decay of its parent ^{226}Ra). Measurements at a large number of stations from throughout the world ocean reveal that on the average about three quarters of the equilibrium amount of radon atoms are present in surface water. The remaining one quarter escape to the atmosphere. This means that the probability of escape is about one third the probability of radio decay. As the mean life of a radon atom with regard to radio-decay is about 5.6 days, the mean lifetime with regard to escape must be about 17 days. The mean thickness of the wind stirred upper ocean at these stations averaged 54 meters. The gases in one seventeenth of this (a layer three meters thick) are replaced each day. However, one correction must be made when this radon-based result is to be applied to other gases such as CO_2. The rate escape of a gas is related to its molecular diffusivity in water: the higher its diffusity, the greater its escape probability.

Keeling's World Problems

1. If your car gets 30 miles to a gallon of gasoline, how many pounds of CO_2 gas does it release to the atmosphere per mile driven? (assume that gasoline has a density of 0.8 gm/cc, and a chemical formula with twice as many hydrogen atoms as carbon atoms). If you were to drive your car 20,000 miles each year, how many tons of CO_2 would you produce annually? If all 5.5 billion people on the planet were to drive cars 10,000 miles in each year, how many gigatons of carbon would be produced? How does this compare to today's fossil fuel CO_2 production rate of ~6 gigatons per year? (1 gallon = 3.785 liters, one ton = 10^6 gm, one pound = 453 gm).

2. For the year 1993, the CO_2 content of the atmosphere averaged globally was about 358 ppm by volume. What would the CO_2 content be 100 years from now (i.e., in the year 2093) if:

   a. CO_2 production remained constant at 6.0 GtC/yr.

   b. CO_2 production rose at the rate of 1% per year.

   Assume that 55% of the CO_2 produced remains in the atmosphere.

3. What would the radon based estimate for the invasion rate of CO_2 into the sea be if the ratio of the mean measured concentration of radon in the surface mixed layer to that if no radon were lost to the atmosphere were 0.60 (instead of 0.77) and the mean thickness of ocean mixed layer were 70 meters (instead of 54 meters). Give your answer in units of moles/m^{2}yr μatm. What would be the invasion rate of CO_2 at 280 μatm? If this were the true CO_2 invasion rate, then what would be the pre-nuclear ratio of the $^{14}C/C$ in mean surface water ΣCO_2 to $^{14}C/C$ in the atmosphere have been?

4. Assume that as of 1990 the total amount of fossil fuels burned since the beginning of the Industrial Revolution was 230 gigatons. Assuming that all this CO_2 remained in the atmosphere (i.e., no transfer into the ocean or into the terrestrial

biosphere), calculate the expected atmospheric CO_2 content in 1990. Assuming that fossil fuel carbon has an average $\delta^{13}C$ -27‰ and that no isotopic exchange of atmospheric carbon with either oceanic or biospheric carbon occurred, by how many ‰ ratio have dropped? Assume that as of 1950, a total of 70 gigatons of carbon had been added to the atmosphere as a result of fossil fuel burning since the beginning of the Industrial Revolution. Assuming that the fossil fuels are free of radiocarbon and again no isotopic exchange of atmospheric carbon with either oceanic or biospheric carbon occurred, by how many ‰ should the atmospheres $^{14}C/C$ ratio have dropped by the year 1950? Calculate the following ratios:

a. $\dfrac{\text{Actual } CO_2 \text{ rise 1850 to 1990}}{\text{Expected rise if all fossil fuel } CO_2 \text{ remained airborne}} = \_\_\_\_$

b. $\dfrac{\text{Actual } ^{13}C/^{12}C \text{ drop 1850 to 1990}}{\text{Expected drop if no isotopic exchange with carbon in other reservoirs}} = \_\_\_\_$

c. $\dfrac{\text{Actual } ^{14}C/^{12}C \text{ drop 1850 to 1950}}{\text{Expected drop if no isotopic exchange with carbon in other reservoirs}} = \_\_\_\_$

The definitions of $\delta^{13}C$ and $\Delta^{14}C$ are as follows:

$$\delta^{13}C = 1000 \text{ x } \frac{(^{13}C/^{12}C_{atm} - {}^{13}C/^{12}C)_{\text{mean ocean}}}{(^{13}C/^{12}C)_{\text{mean ocean}}}$$

$$\Delta^{14}C = 1000 \text{ x } \frac{(^{14}C/C_{atm} \quad {}^{14}C/C)^{1850}_{atm}}{^{14}C/C\,^{1850}_{atm}}$$

Both are akin to percentage differences from the ratio measured in a reference material. But they are given in parts per thousand instead of parts per hundred.

Assume that in 1850 the atmosphere contained 550 gigatons of carbon and that this CO_2 had a $\delta^{13}C$ value of -6.5‰.

5. Calculate the composition of sea water at equilibrium with an atmosphere with a CO_2 partial pressure of 560 μatm. Assume sea water to be borate free and to have

an alkalinity equal to 2100 µmol/kg and a K_c value of 1445. You can get the answer either by trial and error or as by solving a quadratic equation. For the former, guess at a $CO_3^=$ concentration. Then use the charge balance equation to calculate the corresponding HCO_3^- concentration. Then substitute both in the equilibrium constant equation (along with CO_2 = 20 µmol/kg).

<u>Example</u>:

guess $CO_3^=$ = 100 µmol/kg

then HCO_3^- = 2100 - 2 x 100 = 1900

and $K_c = \frac{1900 \times 1900}{20 \times 100} = 1805$ Too high!

so choose a larger $CO_3^=$ ion concentration

and repeat until K_c = 1445.

6. Explain why it is that burning of fossil fuels causes the atmospheric O_2 content to drop 13.5 µatm for every 5.5 µatm CO_2 rises, when for plant growth or plant respiration this ratio is very close to 1.

7. Explain the difference between the atmospheric radiocarbon records for the northern and southern hemispheres. Why the annual wiggles in these curves?

8. If the surface water bomb radiocarbon excess at the time of the GEOSECS survey had averaged 80‰ (instead of 160 ‰) greater than the prenuclear $\Delta^{14}C$ value (and if the mean penetration depth were the same as shown on page 29), which of the parameters in the simple model shown at the top of page 28 would have to be changed? What would its new value be? How would the ocean inventory of bomb radiocarbon atoms have differed?

9. Plants living in the surface sea produce O_2 gas. These new molecules eventually escape to the atmosphere. If the piston velocity for O_2 is 3 meters/day and the mean thickness of the mixed layer is 54 meters, how many days does the average O_2 molecule remain in the sea before escaping to the atmosphere?

10. The simple model shown on p. 28 predicts that during the 1980s the global mean air-sea CO_2 difference should have averaged 8µatm (see pg. 40). Let's say that marine chemists had succeeded in measuring this difference at enough places and seasons to convince the world that the true difference was only 4±1 µatm. How might this difference be explained?

11. Had the measurements made during the GEOSECS survey have indicated that the mean penetration depth of bomb radiocarbon tritium were ~720 meters instead of ~360 meters, then what would be the minimum amount of fossil fuel CO_2 taken up by the ocean at a time when the atmosphere was rising 3.0 GtC/year?

12. Planet X is identical to the Earth in most respects (same ocean and continent areas, same ocean and atmosphere chemistry as that for the preindustrial earth, same size atmosphere). One important difference exists; the mean depth of its ocean is only 475 meters (compared to 3800 for the Earth). Three hundred gigatons of carbon are released as CO_2 through the burning of fossil fuels. No nuclear bombs are exploded nor nuclear reactors operated. Several hundred years later, this extra CO_2 has become thoroughly equilibrated with Planet X's ocean and terrestrial biosphere. Calculate the following quantities:

    a. The atmospheric $^{14}C/C$ reduction (assume that fossil fuels are radiocarbon free)

    b. The atmospheric $\delta^{13}C$ change (assume that it started at -6.5‰ and that the carbon isotope composition of fossil fuel carbon is -26.5‰)

    c. The atmospheric CO_2 content (assume that it started at 280µatm)

    Give your answers as follows:

    a. $\frac{^{14}C/C_{After}}{^{14}C/C_{Before}}$ = ____________________

    b. $\delta^{13}C_{Before} - \delta^{13}C_{After}$ = ____________________ ‰

c. pCO_{2After}^{atm} = ______________________________ μatm

The total mass of the biosphere (wood, soils...) is 1000 gigatons. Assume for simplicity that prior to Planet X's industrial revolution, its ocean and biosphere had uniform $^{14}C/C$ ratios equal to that in the atmosphere. Assume that the ocean has a uniform ΣCO_2 concentration of 1.91 moles/meter^3. The area of Planet X is 5.1 x $10^{14}m^2$, that of the ocean is 3.6 x $10^{14}m^2$. Assume for simplicity that the ocean has the same $\delta^{13}C$ as fossil fuels. Assume no change in biosphere size. Assume a borate free ocean with preindustrial $[CO_2]$ = 10μmol/liter, $[HCO_3^-]$ = 1700μmol/liter and $[CO_3^=]$ = 200μmol/liter. The equilibrium constant, K_c, is 1445. Do a and b first. They are relatively easy. By contrast, c is quite difficult. If you can't get c, just write down the equations.

13. If in the year 1800 A.D., forests covered one third of the Earth's land area, and if their total tree biomass was 600 GtC, how many grams of carbon were there per square centimeter forest? How many tons of biomass per hectare (a square hectare measures 100 meters on a side)? Trees can be thought of as umbrellas which when folded up become cylinders extending 20 meters above ground and 10 meters below ground with a uniform diameter equal to that of the trunk (assume it to be 50 cm). If so, on the average, how many trees would there be per hectare? Assume the density of wood to be 0.9 gm/cm^3.

14. The UN mandates that enough trees be grown such that 30 years from now the added biomass will be 60 GtC. If these trees achieve the mass given in problem #13, how many will there be? If they are spaced as in problem #13, how many hectares will be required? What fraction of the Earth's land area will this require? Three people can be supported by the food grown on a single hectare. If existing farm land were used to grow these trees, what fraction of today's farm land would this require? (Assume the population to be 5.6 billion)

15. Assume that Biosphere 2 has an area of 2 hectares and a mean height of 10 meters. Further, assume that its soils contain 2.8 gmC/cm^2 but that the vegetation can support at steady state only 0.8 gmc/cm^2. The soils cover 80% of the area of Biosphere 2. Further, assume that all the organic matter is of the 'active' variety and has a survival (i.e. replacement) time of 20 years. Still further, assume that the standing biomass of vegetation is at steady state (i.e. it is neither increasing or decreasing) and that the concrete has been sealed so that it no longer takes up CO_2. On January 1, 1994, the pO_2 was 210,000 μatm and the pCO_2 was 2000 μatm. The ratio of CO_2 creation to O_2 consumption is one mole per mole. If no remedial action were taken, how would these values change over the course of one year (i.e., what would they be as of January 1, 1995?) If instead, the Biospherians had an apparatus which allowed them to remove CO_2 by reacting it with CaO stored in anticipation of this problem, how much $CaCO_3$ would they form in the course of the year in order to maintain the initial CO_2 content of their air? If they had a second piece of apparatus which electrolized water to form H_2 and O_2, how much water would they have to electrolize during the course of the year in order to maintain the O_2 content of the air at its initial value? A gigantic problem associated with this solution would be what to do with the H_2 gas. Assuming that it could be kept separate from the O_2 generated and transferred into a balloon mounted above the roof of Biosphere 2, what would be the ratio balloon volume to the Biosphere 2 volume at the end of one year? (Assume that both the balloon and Biosphere 2 are at one atmosphere pressure).

16. Assume that over the course of the year the average daytime photosynthetic production of organic C is three times the consumption rate of excess soil carbon by bacteria. If the biomass of Biosphere 2 is to be at steady state, this creation of new biomass must be exactly balanced by oxidation of old biomass. One difference: assume that respiration occurs at a uniform rate round the clock (i.e., no diurnal

cycle) but photosynthesis occurs only during an 8-hour period from 8 am to 4 pm (i.e., it is shut down during the other 16 hours). If on a typical morning at 8 am the CO_2 partial pressure in Biosphere 2 air is 2500 μatm, what will it be at 4 pm when photosynthesis stops? The volume occupied by one mole of air at one atmosphere pressure and 25°C is 24.6 liters.

Super Problem

In the year 2401, David Ralph Keeling, a distant descendant of the clan made famous in the 20th century by their measurements of CO_2 and O_2 in the Earth's atmosphere, is sent to assess what terrible fate befell a colony established by biospherians sent forth from Earth in the year 2081 to Kri, a planet of the neighboring star Ciolki. After three centuries of what seemed to be an extraordinarily successful venture, radio communication abruptly ceased. Twenty years have passed since this last report was transmitted. As he steps forth from his speed-of-light space ship, young Keeling is struck by a horrible stench. Hulks of dead animals and plants strew the landscape. A quick survey by rotocoptor confirms that some catastrophe must have struck down all life on the planet. Only the most primitive of bacteria appear to have survived; they slowly devour the rotted remains.

Dee-Ar, as he is known to his friends, has been assigned by the expedition leader to assess whether this disaster could be related to the heavy exploitation of Kri's vast graphite reserves. While the colony was established by 8 biospherians, its population soared to a staggering 4 billion just before the catastrophe struck.

Question #1: Assuming that the catastrophe happened exactly 300 years after the first group of 8 babies were born, if every woman on planet Kri gave birth to one set of quadruplets (2 boys and 2 girls) and if everyone lived to the age of 80, then what was the designated child-bearing age?

Dee-Ar's task is complicated by the fact that the Krians were very secretive about their affairs. Communications with Earth were restricted to the bare minimum of information agreed upon before the original biospherians were forced to leave Earth. And try as he may, Dee-Ar can locate no records what-so-ever concerning Kri's carbon cycle. The only information comes from measurements made by the expedition team. Kri was selected for colonization because it so closely resembled Earth in size and surface character. Its ocean covers almost half the planet and its atmosphere exerts a pressure of 1000 gm/cm^2 and is made of 20% O_2 and 80% N_2. The CO_2 pressure measured by the investigation team is 4000 µatm. Based on the number of graphite burning power plants Dee-Ar sees during his overflight, he is convinced that the CO_2 pressure must now be a good bit higher than it was prior to colonization. Further, the absence of any mountain glaciers puzzles him, for clear evidence of fresh morraines as much as 2 kilometers below the tops of the highest peaks is noted by the expedition's geologist, Dr. Dentons. Had the descendants of the biospherians created so large a greenhouse warming that these glaciers melted away in a span of just 300 years? A further clue comes from the tropics where temperatures now average 40°C. The remains of abandoned cities demonstrate to Dee-Ar that the tropics were once inhabited. Did a greenhouse warming drive people to higher latitudes? Fortunately, Kri's equatorial plane is alined with its orbit; otherwise, hot summers would have made even temperate latitudes unsuitable for agriculture.

Dee-Ar rues the absence of glaciers, for they would have archived both the post-colonization CO_2 rise and O_2 decline. Then an idea came to him. Maybe the $^{14}C/C$ and $^{13}C/C$ ratios in trees might provide the needed information. Dee-Ar first makes measurements on matter from plants killed by the catastrophe, on CO_2 from Kri's air and on ΣCO_2 from Kri's sea. He finds:

	$\delta^{13}C$*	$\frac{^{14}C/C^{**}}{^{14}C/C_{stan.}}$
Atm CO_2	-15‰	.75
Ocean ΣCO_2	6‰	.75
Trees	-33‰	.75

*Relative to Earth PDB

**Relative to Earth 1850 (normalized to wood remove effects of stable isotope fractionation)

He repeats these measurements at various locations and depths in the ocean and finds to his surprise that they are everywhere the same. "My, such rapid air-sea CO_2 exchange and ocean mixing", he muses. As the biospherians had been banned from Earth because of their violent stand against both nuclear power and nuclear weapons, Dee-Ar feels safe to assume that no man-made ^{14}C is present on Kri.

Of course, by themselves, these measurements provide no information regarding perturbations in Kri's carbon cycle resulting from colonization. Then Dee-Ar lucks out. He finds a large tree (now leafless) fenced off and marked with a plaque, which reads "Planted in 2090 from a seedling carried to Kri from Earth. Although a tropical species devoid of rings, Dee-Ar is confident that he can construct a rough time scale based on the radial distance from the tree's center. He measures both carbon isotope ratios at frequent increments along a radial traverse. He is pleased by the results.

For the inner-most three quarters of the boring, the ratios remain nearly uniform. Then, in the outer quarter, both ^{14}C and ^{13}C show an exponential drop. The values for the pre-colonization steady state are

$$\delta^{13}C = -22\%$$

$$^{14}C/C = 1.5\ ^{14}C/C\ \text{1850 earth wood}$$

To aid in the interpretation of these results, Dee-Ar makes the following measurements

$$\Sigma CO_2^{sea} = 10{,}000\ \mu\text{mol/liter}$$

$$\text{Mean depth sea} = 380\ \text{meters}$$

$$\text{Area of sea} = 2.5 \times 10^{14}\ m^2$$

$$\text{Volume of sea} = 9.5 \times 10^{16}\ m^3$$

He also makes a rough estimate that the terrestrial biomass (now all dead) was, prior to the catastrophe, about 500 GtC. As Kri was devoid of life before colonization, this 500 GtC must have been produced during the last 300 years. Dee-Ar further assumes that its half replacement time was 25 years.

Q-2. From this information, Dee-Ar calculates how much coal was burned. What answer does he obtain?

Dee-Ar's next step is to calculate the expected $^{13}C/^{12}C$ ratio change assuming that the only perturbation is from coal burning. He makes carbon isotope measurements on Kri's graphite and finds that it has a quite uniform ratio of -25‰. At first Dee-Ar is puzzled to see that the ^{13}C decline measured in the tree is smaller than that predicted from his coal consumption estimate. Then he realizes that the difference is the result of biosphere growth and that he can use it to check his rough estimate of Kri's standing biomass.

Q-3. What result does he obtain?

Having established the amount of excess CO_2 added to Kri's atmosphere-ocean system, Dee-Ar's next task is to attempt to reconstruct the pre-colonial CO_2 partial pressure. He equilibrates Kri's sea water with air containing 3600 and 4400 ppm CO_2 and measures the ΣCO_2 in these two sea water samples

p_{CO_2} µatm	ΣCO^2 µmol/liter
3600	9950
4000*	10,000**
4400	10,050

*Kri's atmospheric CO_2 content

**Kri's ocean ΣCO_2

He also demonstrates that the p_{CO_2} and ΣCO_2 of Kri's ocean is everywhere the same.

Q-4. What does Dee-Ar conclude about the pre-colonial atmospheric CO_2 content?