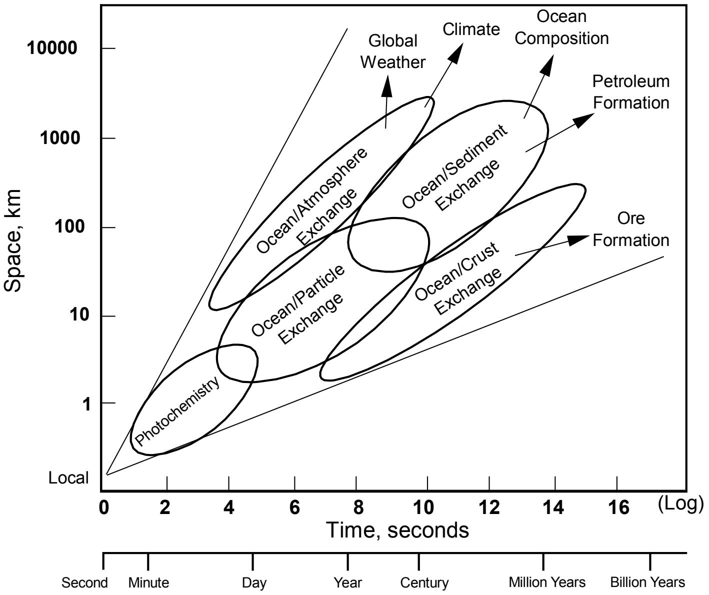
Lecture 1: Introduction

Chemical oceanography is the study of everything about the chemistry of the ocean based on the distribution and dynamics of elements, isotopes, atoms and molecules. This ranges from fundamental physical, thermodynamic and kinetic chemistry to two-way interactions of ocean chemistry with biological, geological and physical processes. It encompasses both inorganic and organic chemistry, and includes studies of atmospheric and terrestrial processes as well. Chemical oceanography includes processes that occur on a wide range of spatial scales; from global to regional to local to microscopic dimensions, and temporal scales; from geological epochs to glacial-interglacial to millennial, decadal, interannual, seasonal, diurnal and all the way to microsecond time scales. The field by its own nature is very much an interdisciplinary field.

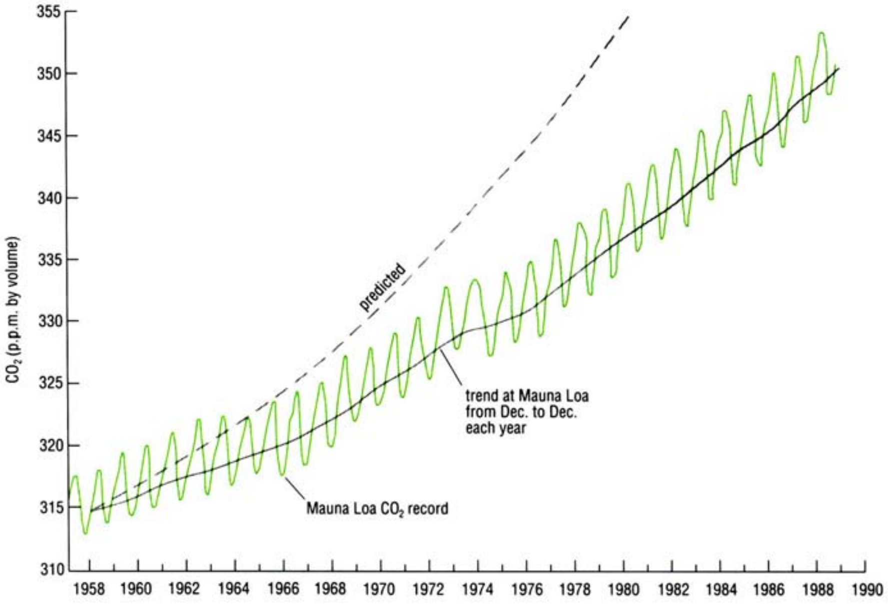


The advantages of the chemical perspective include:

1. Huge information potential due to large number of elements (93), isotopes (260), naturally occurring radioisotopes (78) and compounds (innumerable) present in the ocean.
2. Chemical measurements in the ocean are highly representative, reproducible and predictable (statistically meaningful). One drop of water is about 1/20th of a milliliter or 0.05 g, this is 2.8×10^{-3} moles or 1.7×10^{21} molecules.
3. Quantitative treatments are possible (stoichiometries, balances, predictions of reaction rates and extents).
4. We can learn about processes from chemical changes. Seawater composition integrates multiple previous events, this is important because most of the ocean is inaccessible to direct observation.

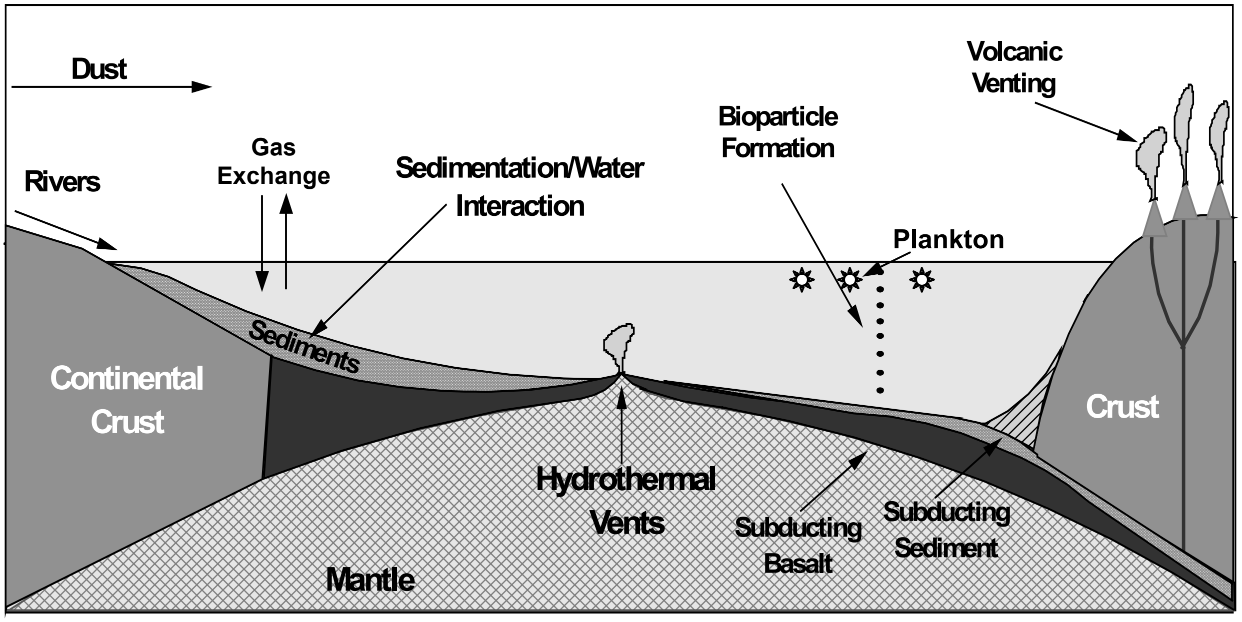
How and Why is This Field Relevant?

We are all aware of the CO_2 and other greenhouse gases increase in the atmosphere since the beginning of the industrial revolution. This is seen in the classic data from C.D. Keeling (1976) showing the seasonal oscillations and the steady annual increase of CO_2 at the Mauna Loa Observatory. Most experts conclude that we are already witnessing the impact of this as global warming, and the signal is expected to become increasingly more pronounced.



The inventory of dissolved inorganic C in the oceans is 50-60 times greater than that in the atmosphere, so a small perturbation of the ocean carbon cycle can result in a substantial change in the concentration of CO_2 in the atmosphere. The ocean carbon cycle influences atmospheric CO_2 via changes in the net air-sea CO_2 flux that are driven by differences in the partial pressure of CO_2 between the surface ocean and atmosphere. This exchange process is dominated by two interdependent "carbon pumps" that deplete the surface ocean of total CO_2 relative to deep water. Because the solubility of CO_2 increases with decreasing temperature, the **SOLUBILITY PUMP** transfers CO_2 to the deep sea during formation of cold deep water at high latitudes. **This is a link of the ocean carbon cycle to physical processes (circulation)**. At the same time the **BIOLOGICAL PUMP** removes carbon from surface waters by settling of organic and inorganic carbon derived from biological production to the deep sea. **This is a link of the ocean carbon cycle to biological processes**.

Understanding the natural processes that affect the global carbon cycle is an important requisite for correctly predicting the effects of global warming. For this we need a sound descriptive and quantitative background in all aspects of chemical oceanography and a good understanding of the coupling between chemical oceanography, tectonics, climate, and physical, and biological oceanography. As illustrated in the figure below the oceans are in continues contact with the atmosphere, lithosphere and biosphere.



In addition to the major role the ocean plays in the global carbon cycle the world's ocean is also a resource for minerals, energy (gas and petroleum), fisheries, and is the ultimate water source.

Overview of Ocean Chemistry

Chemical Oceanography is the most interdisciplinary of all the sub-disciplines of ocean sciences. The above figure illustrates some of the interactions between the oceans (hydrosphere), lithosphere, atmosphere and biosphere.

- Chemical components of the ocean influence the density of seawater and thus effect its circulation.

- Biological processes in the ocean are controlled by the chemistry (nutrient availability). At the same time biological processes are an important control on chemical distributions. The synergy between biology and chemistry has led to a whole new thriving sub-discipline called biogeochemistry.

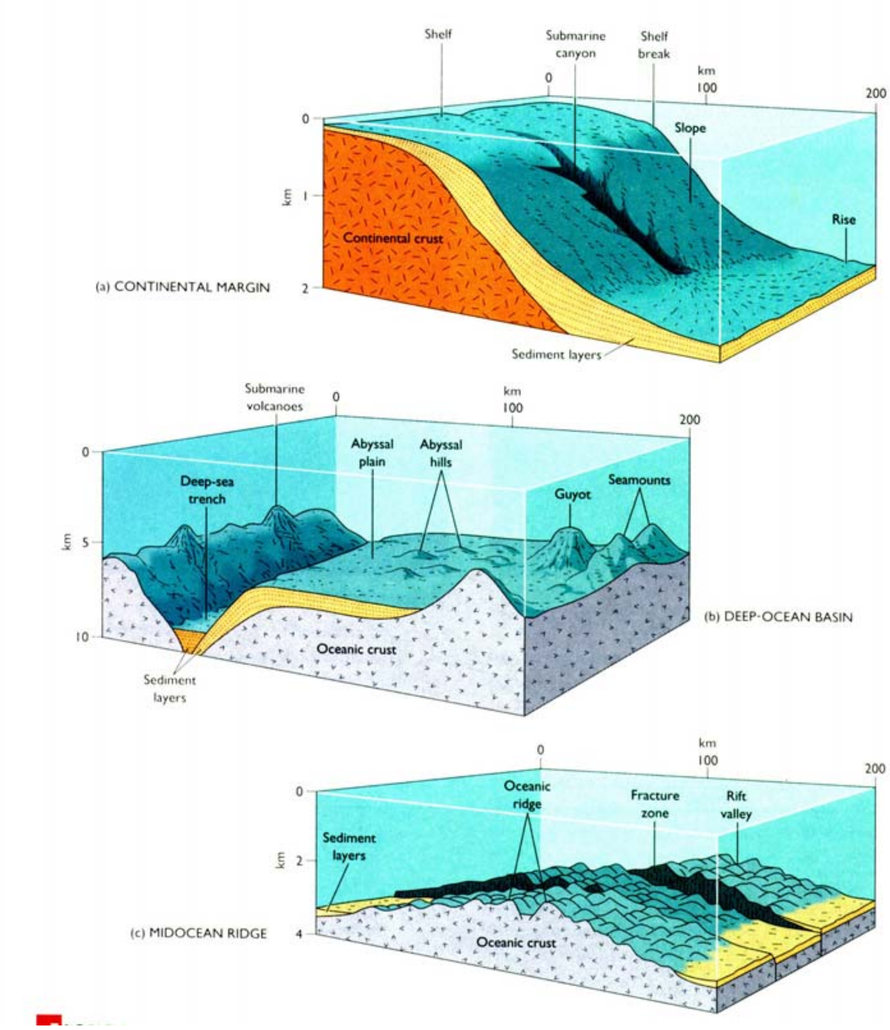
- Chemical components are tracers of physical, biological, geological and chemical processes. Understanding what controls chemical distributions helps us understand ocean dynamics.

- Oceanic – Crustal coupling control the distribution of many ions in seawater on time scales of 10^4 to 10^6 years. Thus, we can learn from ocean chemistry about weathering, hydrothermal activity, and other crustal processes.

- Chemical components of marine sediments provide clues necessary to unravel the history of past ocean chemistry and ocean-atmosphere dynamics. Understanding the past should help us predict the future.

Some Descriptive Oceanography

The topography and structure of the ocean floor are highly variable from place to place and reflect tectonic processes within the Earth's interior. These features have varied in the past so that the ocean bottom of today is undoubtedly not like the ocean bottom of 50 million years ago. Even as short as about 5 million years ago Central America did not exist and there was an open seaway between the Atlantic and Pacific. The major topographic systems, common to all oceans, are the continental margins, the ocean-basin floors and the oceanic ridge systems. Tectonic features such as fracture zones, plateaus, trenches and mid-ocean ridges act to subdivide the main oceans into a larger number of smaller basins.



The continental margin regions are the transition zones between the continents and ocean basins. The general features of continental margins may be one of two sequences: shelf-slope-rise-basin or shelf-slope-trench-basin.

The continental shelf is the submerged continuation of the adjacent land, modified in part by marine erosion or sediment deposition. The seaward edge of the continental shelf can frequently be clearly seen and it is called the shelf break. The shelf break tends to occur at a depth of about 200 m over most of the ocean. On average, the continental shelf is about 70 km wide, although it can vary widely (compare the east coast of China with the west coast of Peru).

The continental slope is characterized as the region where the gradient of the topography changes from 1:1000 on the shelf to greater than 1:40. Thus continental slopes are the relatively narrow, steeply inclined submerged edges of the continents.

The ocean trenches are the topographic reflection of the subduction of oceanic plates beneath the continents. The greatest ocean depths occur in such trenches. The deepest is the Challenger Deep, which descends to 11,035 meters in the Marianas Trench.

The continental rises are mainly depositional features that are the result of coalescing of thick wedges of sedimentary deposits carried by turbidity currents down the slope and along the margin by boundary currents. Deposition is caused by the reduction in current speed when it flows out onto the gently sloping rise. Gradually the continental rise grades into the ocean basins and the abyssal plains.

The average depth of the oceans is 3730 m. The area, volume and average depth of the ocean basins and some marginal seas are given below. The Pacific Ocean is the largest and contains more than one-half of the Earth's water.

Region	**Area** (10^6 km^2)	**Mean Depth** (m)	**Volume** (10^6 km^3)
Pacific Ocean	165.25	4282	707.56
Atlantic Ocean	82.44	3926	323.61
Indian Ocean	73.44	3963	291.03
Arctic	14.09	1205	16.98
South East Asia Seas	8.14	1212	9.87
Central America Seas	4.32	2216	9.57
Mediterranean Sea and Black Sea	2.97	1429	4.24
Hudson Bay	1.23	128	0.16
Other Marginal Seas (Baltic, Red etc.)	9.18		7.3

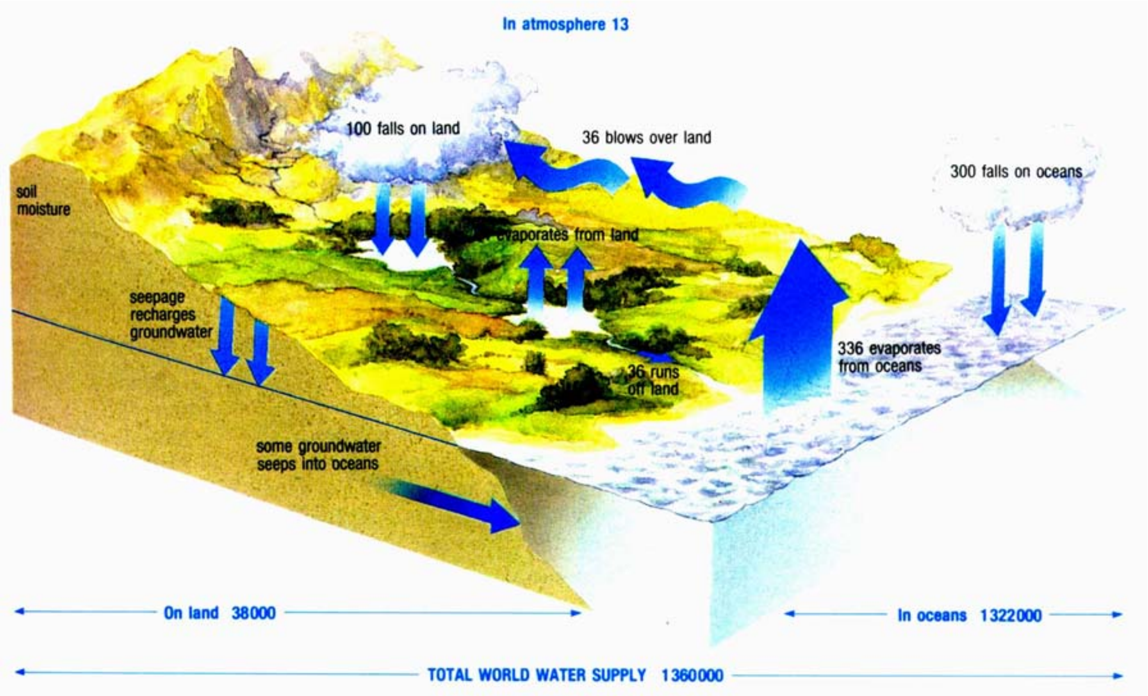
Global Water Cycle

Water is present on Earth in three phases - solid, liquid and gas. The ocean contains the bulk (97%) of the earth's water (1.37 x 10^9 km^3 or about 1.37 x 10^{24} g) and moderates the global water cycle. Glaciers are the second largest reservoir with about 2% of the total. The reservoir of water in rivers, lakes and the atmosphere is a trivial part of the total (0.003%). A summary of the water reservoirs is given below (after Reeburgh, 1997; Berner and Berner, 1987).

Environment	**Water Volume** (km^3)	**Percentage of Total** (%)
Surface Water		
Freshwater Lakes	125,000	0.01
Saline Lakes and Inland Seas	104,000	0.009
Rivers and Streams	1,200	0.0001
Total	230,000	0.0191
Subsurface Water		
Soil Moisture	67,000	0.005
Ground Water (shallow, <750m)	4,000,000	0.30
Ground Water (deep, 750-4000m)	5,000,000	0.38
Total	9,067,000	0.685
Ice Caps and Glaciers	29,000,000	2.05
Atmosphere	13,000	0.001
Biosphere	600	.00004
Oceans	1.37 x 10^9	97.25
Total	1.408 x 10^9	

Water is continually moving between reservoirs as part of the hydrological cycle. These fluxes are summarized in the figure and table below. Evaporation exceeds precipitation over the ocean, while precipitation exceeds evaporation over land. River flow from land to the ocean accounts for the difference.

Flux	**Water Flux** (km^3 yr^{-1})
Ocean Evaporation	423,000
Ocean Precipitation	385,600
Land Evaporation	72,900
Land Precipitation	110,300
Runoff from Land	37,400



The ocean has a turnover time of about 37,000 years with respect to river inflow. This is how long it would take to fill the ocean if it were totally dry. Turnover times are defined as the mass in the reservoir divided by the input or removal rate. By comparison the average residence time of water in the atmosphere with respect to evaporation from the oceans and continents is only about 10 days.

The ocean's role in controlling the water content of the atmosphere has important implications for past, present and future climates of the Earth. Water vapor itself is the most important greenhouse gas and, alone, is responsible for about 23°C of greenhouse warming. Without any greenhouse gases the average earth temperature would be 260°K. Instead it averages 283°K mostly because of the trapping of infrared radiation by water vapor. Water's unusually high heat capacity and latent heat of evaporation play an important role in heat storage and transport.

History

Much of the early history of oceanography was descriptive and chemical oceanography was considered part of biological oceanography until the 1960's. The stature of chemical oceanography grew as it was realized that chemical tracers had the power to answer problems in all disciplines of oceanography. By the 1970's the basic distribution of most elements in seawater had been fairly well understood. At that time the sub-discipline of marine chemistry emerged. These chemists focused their efforts on understanding chemical reactions and mechanisms in the ocean and at its boundaries.

Some especially noteworthy events include:

1772 Lavoisier produced the first respectable analyses of seawater and attempted to isolate some of its constituent salts.

1836 Gay-Lussac showed that the total salt content of the ocean was remarkably constant throughout the Atlantic. He suggested that the small differences that did exist were due to variations in river runoff as well as evaporation and precipitation

1819 Marcet analyzed seawater from several different locations and determined that there was a constant proportion between the major elements. We now refer to this fundamental concept as the Marcet's Principle or the Principle of Constant Proportions.

1865 Forchhammer presented the first definition of salinity

1884 Dittmar completed the first systematic analyses of the major ions in seawater. He used samples collected during the HMS Challenger Expedition (1873-1876)

1930s Rockefeller Foundation provided support to strengthen oceanographic programs at Scripps Institution of Oceanography, the Woods Hole Oceanographic Institution and the University of Washington.

1940s World War II, which led to the building of the ocean research establishment. Congress created the Office of Naval Research (ONR) in 1946.

1970s International Decade of Ocean Exploration (IDOE) funding of major oceanographic programs (GEOSECS, MANOP, CLIMAP)

1990s Global Change Research Program (GCRP) funding of major programs related to global change (JGOFS, WOCE, TOGA, GLOBEC, RIDGE)

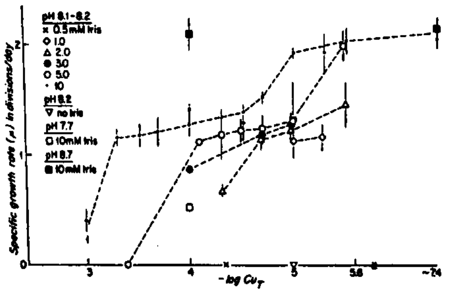
See Pilson (1998, Chapter 1) for more details on the history of Chemical Oceanography.

Scope of Chemical Oceanography: Fundamental Questions

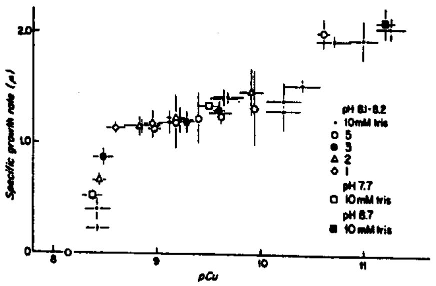
Here are a few examples of some of the key questions addressed in chemical oceanography. From this class you will obtain the tools to address and understand these problems.

- Why is the ocean salty and what controls its salt content? Does evaporation of river water make seawater? The answer is no. Evaporation of river water makes an alkaline lake with pH values ~10 and very low concentrations of calcium and magnesium.

- What are the different forms of chemicals in the oceans and how can we calculate their concentrations using a systematic chemical approach? Copper is toxic to phytoplankton like *Thalassiosira pseudonana*. The growth rate of this organism decreases with increasing total concentration of Cu, but with much scatter in the data (left figure below). When the speciation of copper is taken into account and the activity of the free Cu^{2+} ion is calculated, the scatter is removed (Sunda and Guillard, 1976). The conclusion is that the activity of Cu^{2+} and not the concentration is the main determinant of the toxicity.

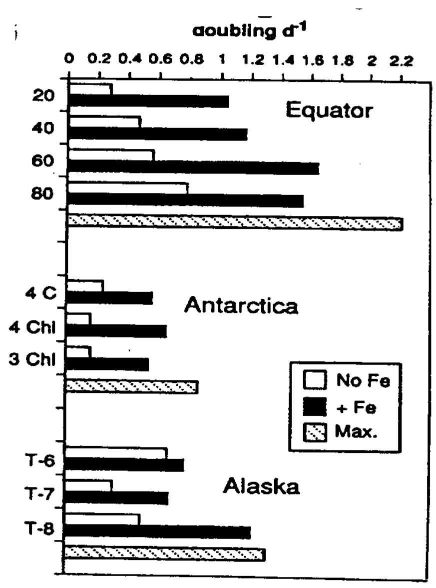


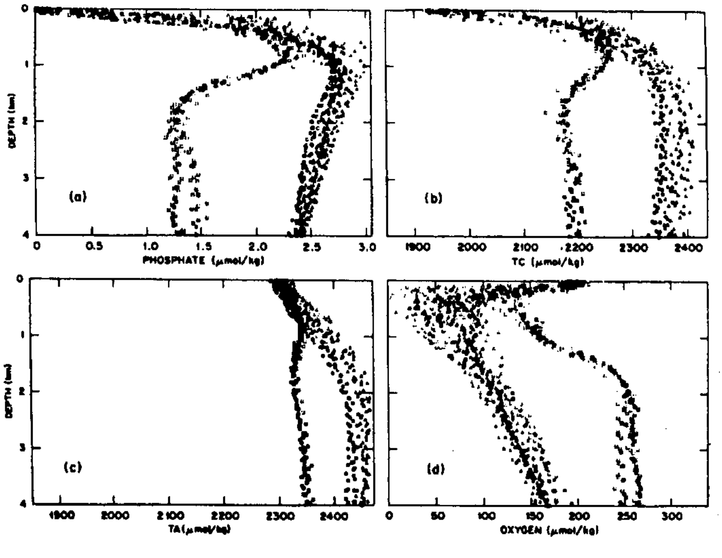
high [Cu] low



high [Cu] low

- What are the chemical controls on biological production and food web structure of the ocean? In some ocean areas iron limits phytoplankton growth. Martin (1991) conducted experiments where he added iron to samples and showed that adding iron stimulated growth rate and also stimulated diatom production.





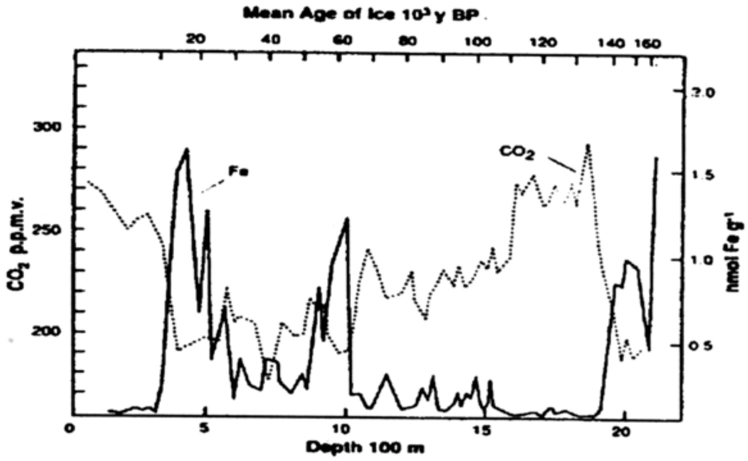
- In what ways do biological processes control the distributions of chemicals in the ocean? Photosynthesis and respiration control the distribution of many elements in seawater.

- What controls the distribution of clay minerals and biogenic phases like calcite ($CaCO_3$), opal (SiO_2) and organic carbon in marine sediments? $CaCO_3$ is enriched in shallow sediments and almost totally absent in deep sediments. A balance between the production of $CaCO_3$ by organisms in the upper water column and dissolution in deeper waters, which is a function of temperature and pressure, controls $CaCO_3$ distribution.

- What can chemical tracers (specific elements and compounds as well as stable and radioactive isotopes) tell us about physical, biological and geological processes and their rates in the ocean? For example, the distribution of ^{14}C and CFCs in seawater can tell as when a water mass was last in contact with the atmosphere thus, the “age” of that water mass and circulation rates.

- How important is the ocean as a sink for fossil fuel CO_2 and other greenhouse gases? Brewer (1978) calculated the pCO_2 in samples from the core of the salinity minimum of the Antarctic Intermediate Water. The youngest samples from further south have highest pCO_2 reflecting the increase in atmospheric CO_2.

- How much has atmospheric CO_2 varied in the geological past and what were the controls? Martin (1991) shows the distribution of iron and CO_2 versus age (0 to 160,000 years BP) in the Vostok ice core in Antarctica. Martin argued that there was increased atmospheric input of dust rich in iron during the last glacial. This stimulated biological production in the ocean and lowered atmospheric CO_2.



The Future

Where do we stand today and what does the future hold? Chemical Oceanography will continue to be an exciting, dynamic and vibrant field as the earth's population struggles to deal with the effects of the increase in fossil fuel CO_2 and other anthropogenic trace gases and global warming. A comprehensive discussion on the future of ocean chemistry research in the US (FOCUS) was recently conducted (Mayer and Druffel, 1999).

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