12.740 Paleoceanography
Spring 2008

Deep Ocean Paleoceanography

12.740 Topic 8 Spring 2008

Benthic Foram Paleoecology I

In the 1970’s, it was hoped that benthic foraminiferal populations could be used in "Imbrie-Kipp" mode to reconstruct deep ocean physical and chemical properties. This idea has been long on hope and slim on results, however.

- There are many more species of benthic foraminifera, but these are scarce compared to planktonic foraminifera (B/P ~ 1%). Studies of benthic foraminifera require much larger samples (10g or more) and take much longer to process and identify.
- Benthic foraminifera do show large-scale variations throughout the present ocean, and temporal changes are recorded in sediment cores. The first studies were of necessity limited to small regions, and the temptation to overdo the planktonic analogy was great; hence depth-correlated changes in the modern ocean were at first attributed to temperature. (e.g. see Streeter, Schnitker studies).
- Subsequent work has shown that, unlike planktonic foraminifera, correlations with temperature do not hold globally. This lack of correlation probably is due to the extremely small range of variation of temperature (a few °C) in the deep ocean. There have been attempts to attribute the observed variations to other deep-water parameters (e.g. oxygen content, carbonate saturation, or even the vaguer term "Uvigerina water" which implies that something in the bottom water controls the Uvigerina population). So far, none of these attempts has a "residence time" of more than a few years. So far, benthic foraminifera have defied a systematic generalization of the factors controlling their species composition. A recent paper by P. Loubere characterizes benthic foram census data from the Pacific in terms of surface productivity and deep water oxygen content.
- It is likely that factors other than deep water properties influence the benthic foraminiferal populations: e.g., food (from the surface) - a correlation between benthic foram flux and productivity has been observed; sedimentation of non-food constituents; other aspects of the sedimentary environment (deep currents, grain size, etc.).

One question of some interest to this "other factors" issue is: where do benthic foraminifera live? If they live at some depth in the sediment, the chemical environment they respond to can be different from those at the bottom of the ocean: while T is the same, the chemical composition of the water, the food sources, oxygen, etc. may differ significantly from that of the bottom water. (To be expanded upon later.)

Benthic Foram Paleoecology II

Few paleoceanographic interpretations based on benthic foraminifera populations survived more than a few years. One partial exception is the study of Streeter and Shackleton (1979) who used glacial increases in the Uvigerina abundance to argue that North Atlantic Deep water ceased or drastically diminished. Although the extent of the decrease is now thought to be considerably less than the foraminiferal populations would suggest, it is agreed that there was less North Atlantic Deep Water in the deepest North Atlantic during glacial times, and so at least the sign was right!

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Streeter and Shackleton, 1979

$\delta\,^{13}C$ as a tracer of deep ocean paleoceanography

The distribution of $\delta^{13}C$ in the modern ocean is linked to oxygen and nutrients.

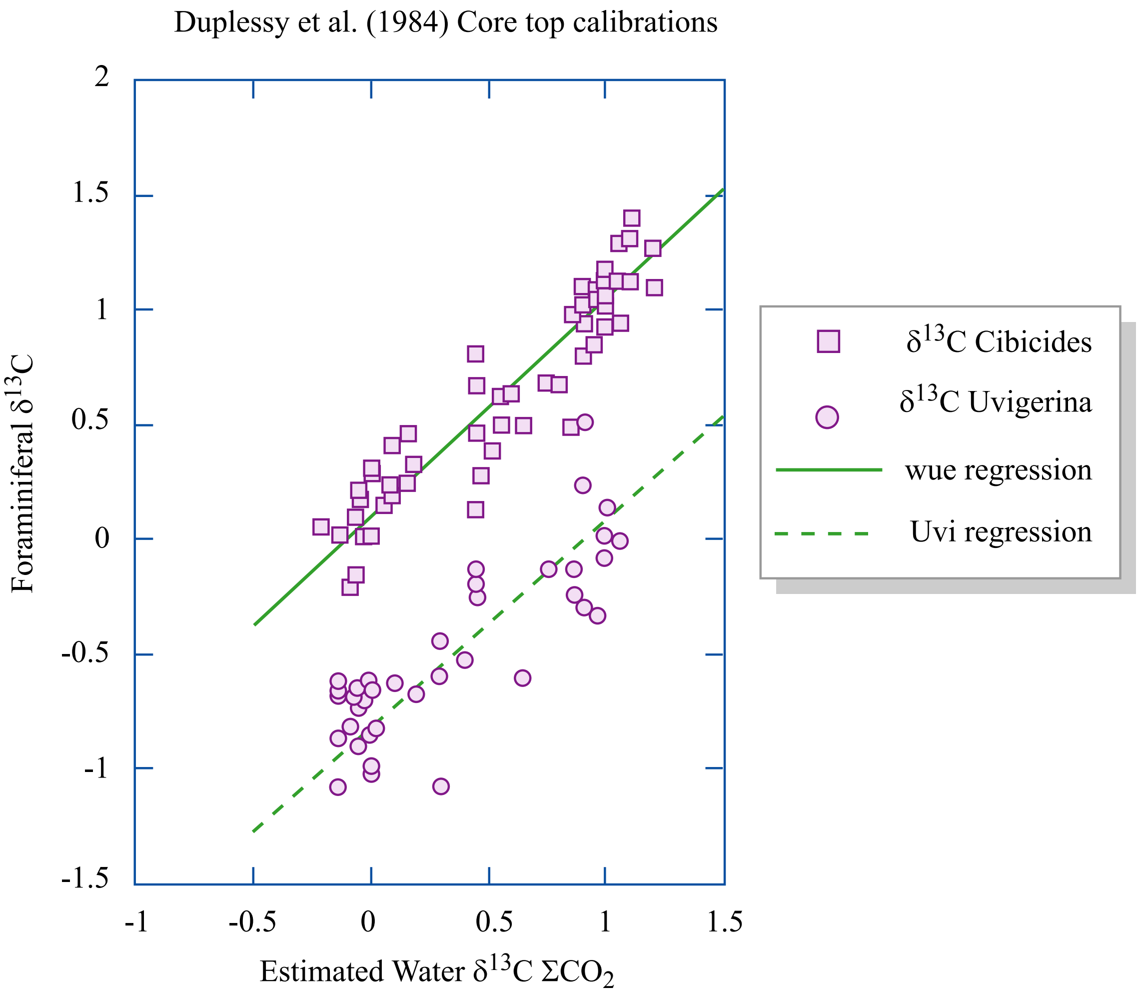
- Organic matter is depleted in ^{13}C. This depletion occurs mainly during the enyzymatic conversion of inorganic CO_2 (itself somewhat depleted related to total dissolved CO_2, which is mainly HCO_3-) to organic matter by plants, mainly a kinetic effect.

Much of the carbon uptake by marine photosynthetic organisms is achieved by the transport of free aqueous CO_2 (which is depleted in ^{13}C by ~10‰) across cell membranes (although there are also some ways to use anionic HCO_3- directly). Furthermore, because CO_2(aq) concentrations are low (10-20 µmol/kg), the cell membrane environment can be depleted in CO_2(aq) during rapid photosynthesis because the conversion of HCO_3- to CO_2. is relatively slow. Enzymatic (Rubisco) and other kinetic effects within plants add to this ^{12}C depletion, resulting in the $\delta^{13}C$ of marine organic ranging from -20‰ (tropical and subtropical waters) to -30‰ (Antarctic).

- When this organic matter sinks into the deep ocean, it quantitatively decomposes (~99% in the whole water column; ~80% in the upper 500 m), releasing the bound C, N, and P in the same ratio, and consuming O_2 from the water in the process. The CO_2 released during this respiration process is depleted in ^{13}C, so that the $\delta^{13}C$ of the deeper water lower than that of the original surface waters. A plot of $\delta^{13}C$ vs. P for the modern ocean is linear.

- Hence it is possible to use the $\delta^{13}C$ distribution in the ocean as a tracer of oceanic water masses.

$\delta^{13}C$ as a tracer of deep ocean paleoceanography III



Core top calibration of Cibicides and Uvigerina for $\delta^{13}C$. Note that measurement precision is better than 0.1‰

Figure by MIT OpenCourseWare.

Duplessy et al. (1984)

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Complication: at least some species (especially Uvigerina), and perhaps all, appear to have variable offsets from bottom water composition related to the productivity of the overlying surface ocean.

Zahn et al. (1987)

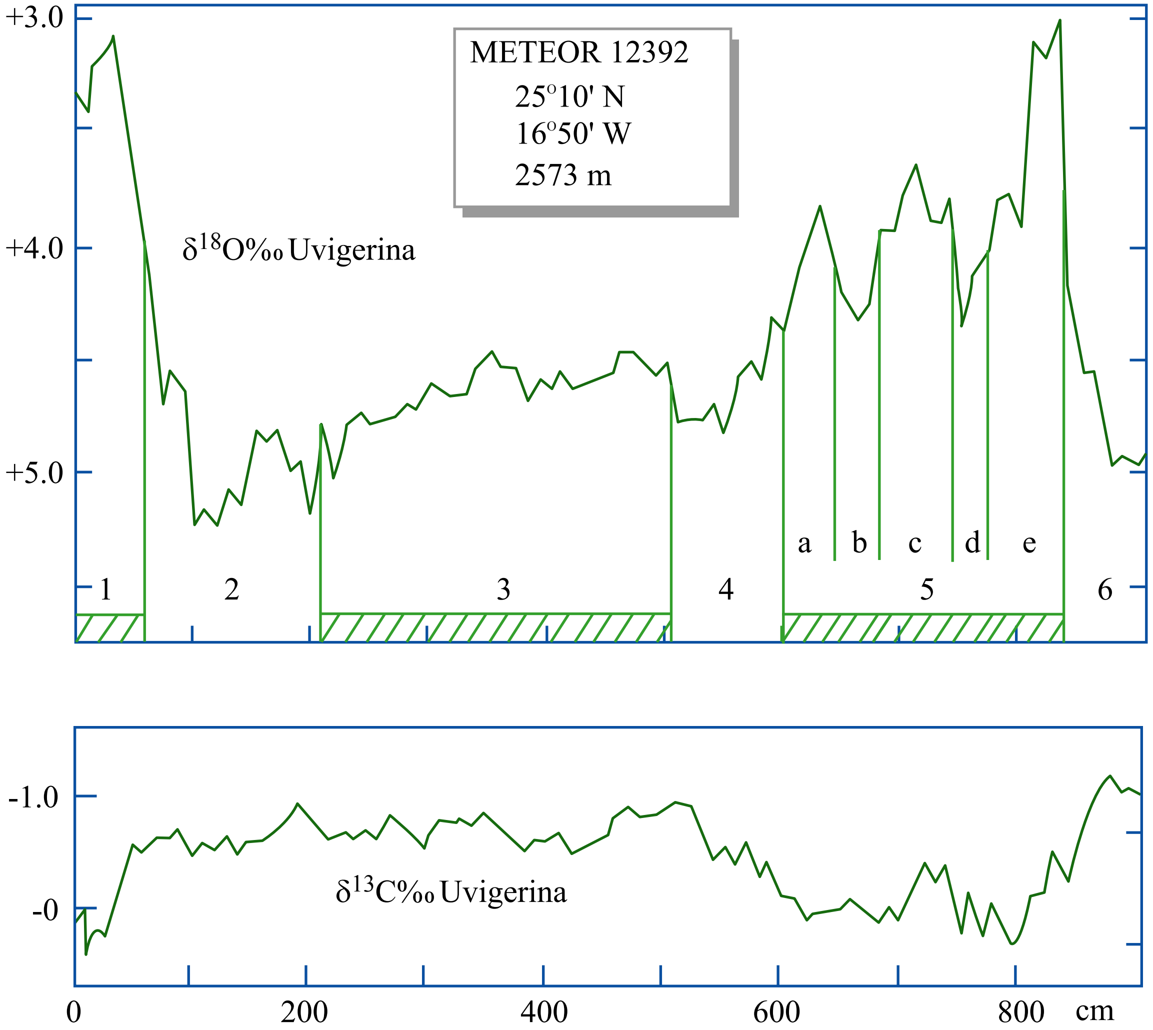
More complications:

- where in the sediment do foraminifera live? If they live at some depth in the sediment, $\delta^{13}C$ can be significantly different from that of the bottom water (e.g. McCorkle et al.).

- The average $\delta^{13}C$ of the ocean is not constant, due to a significant transfer of terrestrial reduced organic into the oceans during glacial periods (tropical aridity and destruction of high-latitude hardwood forests: Shackleton (1977). This means that a local downcore records of $\delta^{13}C$ have a large (and often dominant) component due to changes in the ocean average $\delta^{13}C$, and it is necessary to somehow correct for this in determining the spatial $\delta^{13}C$ distribution at a given time.

Because of these complications, early $\delta^{13}C$ studies of benthic foraminifera were "incomplete interpretations”, modified later. For example, Shackleton (1977) attributed the ^{13}C changes from Uvigerina off Northwestern Africa (core M12392) (almost) solely to changes in the global oceanic $\delta^{13}C$ due to a diminished LGM soil/biospheric carbon reservoir.

Shackleton M12392, off of Northwest Africa



Oxygen isotope and carbon isotope record of core 12392. The section spans about 140 ka.

SHACKLETON(1977), in Fate of Fossil Fuel CO_2

Figure by MIT OpenCourseWare.

Note that this figure is slightly misleading because the "Uvigerina"record is actually a "Uvigerina + Cibicidoides converted to Uvigerina scale" composite record. It turned out later that a lot of the C13 "signal" in this core was due to the variable C13 offset for Uvigerina in high organic carbon glacial sediments (although the "continental biomass" argument is still accepted as part of the benthic C13 record. Later, Shackleton, Imbrie, and Hall (1983) attributed the difference between Atlantic and Pacific records to NADW fluctuations (which would have therefore been a large portion of the total δ^{13}C record in the Atlantic core. Zahn et al. (1986) showed that Uvigerina shows variable δ^{13}C offsets from bottom water that are related to the organic carbon content of the sediment (which they suggested was due to an infernal habitat for Uvigerina). The Northwestern Africa (core M12392) Uvigerina record contains a large component due to organic-carbon source related non-constant δ^{13}C offsets for Uvigerina. Hence the role of NADW fluctuations was smaller than it appeared in the 1983 paper.

Shackleton, Imbrie, and Hall (1983)

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However, so far it appears that the species. *C. wuellerstorfi* records the more reliable record of temporal and spatial variations in C-13 [though even this species also shows negative $\delta^{13}C$ offsets in some environments (e.g. Mackensen, 1993)].

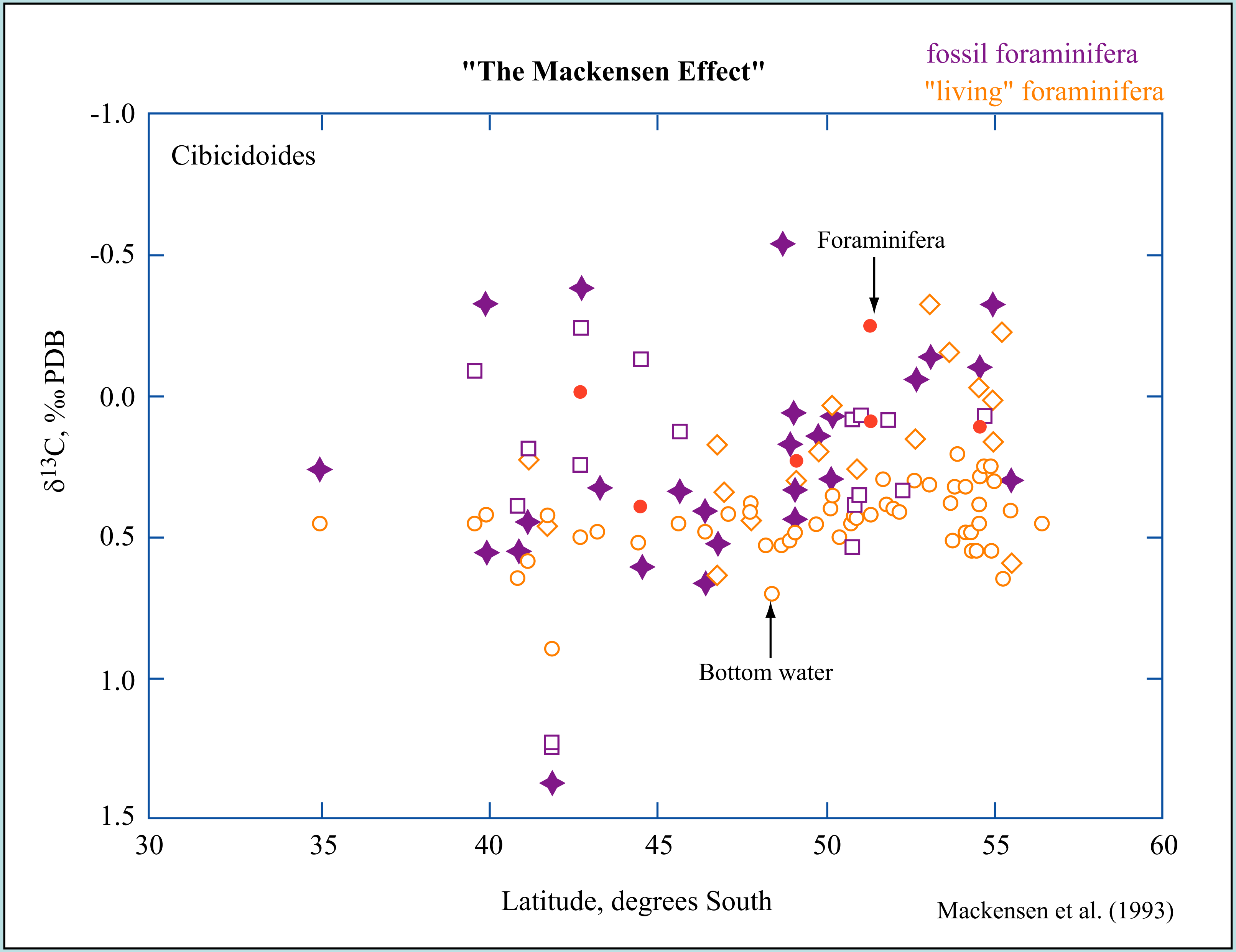

Figure by MIT OpenCourseWare.

Mackensen et al. (1993)

Cd/Ca in foraminifera as a tracer of ocean chemistry and circulation I

Organisms also take up cadmium (Cd) in their organic tissues which is quantitatively released during decomposition just as C,N, and P. Hence Cd plots linearly with P; both are near-zero in subtropical surface waters.

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Boyle (1994)

Cd/Ca in foraminifera as a tracer of ocean chemistry and circulation II

Cd has nearly the same ionic radius as Ca; hence it is well-suited to solid-solution substitution in the calcium carbonate crystal. Chemically, at equilibrium, one would expect that

$$\frac{X_{Cd}}{X_{Ca}} = D_{eq} \frac{\gamma_{Cd}\, f_{Cd}\, [Cd]}{\gamma_{Ca}\, f_{Ca}\, [Ca]}$$

where:

X = the mole fraction of the element in the solid
D_{eq} = the equilibrium constant (distribution coefficient) (determined by the relative free energies of the ion in solution and in the solid)
γ = the activity coefficient of the free ion in solution
f = the fraction of the element that exists in solution as the free ion (i.e., not complexed)
$[\,]$ = the total concentration of the element in solution

For an ideal solid solution (i.e., where the free energy of $CdCO_3$ is the same in solid solution in $CaCO_3$ as it is in pure $CdCO_3$), K_{eq} is equal to the ratio of the solubility products of the pure carbonates $K_{sp}(CdCO_3)/K_{sp}CaCO_3$. (Most solid solutions are non-ideal, however).

Although γ, f, and K are functions of temperature, their temperature dependence is expected to be slight, so that we expect

$$(Cd/Ca)_{carbonate} = D_p\, (Cd/Ca)_{solution}$$

where D_p is the partition coefficient

NaCl crystal structure

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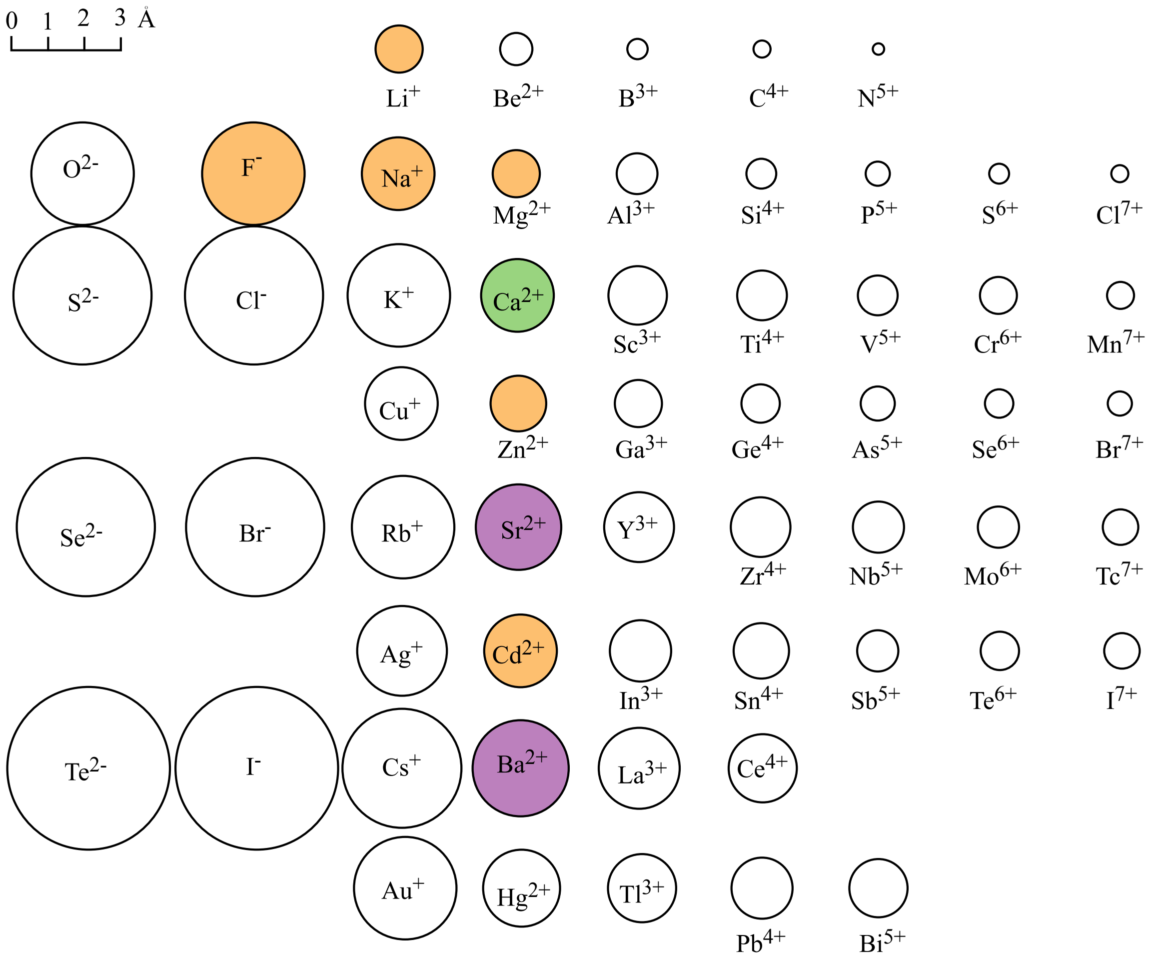
Ionic radii



The relative sizes of different ions (after Pauling).

Figure by MIT OpenCourseWare.

Dependence of ionic radius on coordination # (Shannon)

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G. truncatulinoides ultrastructure

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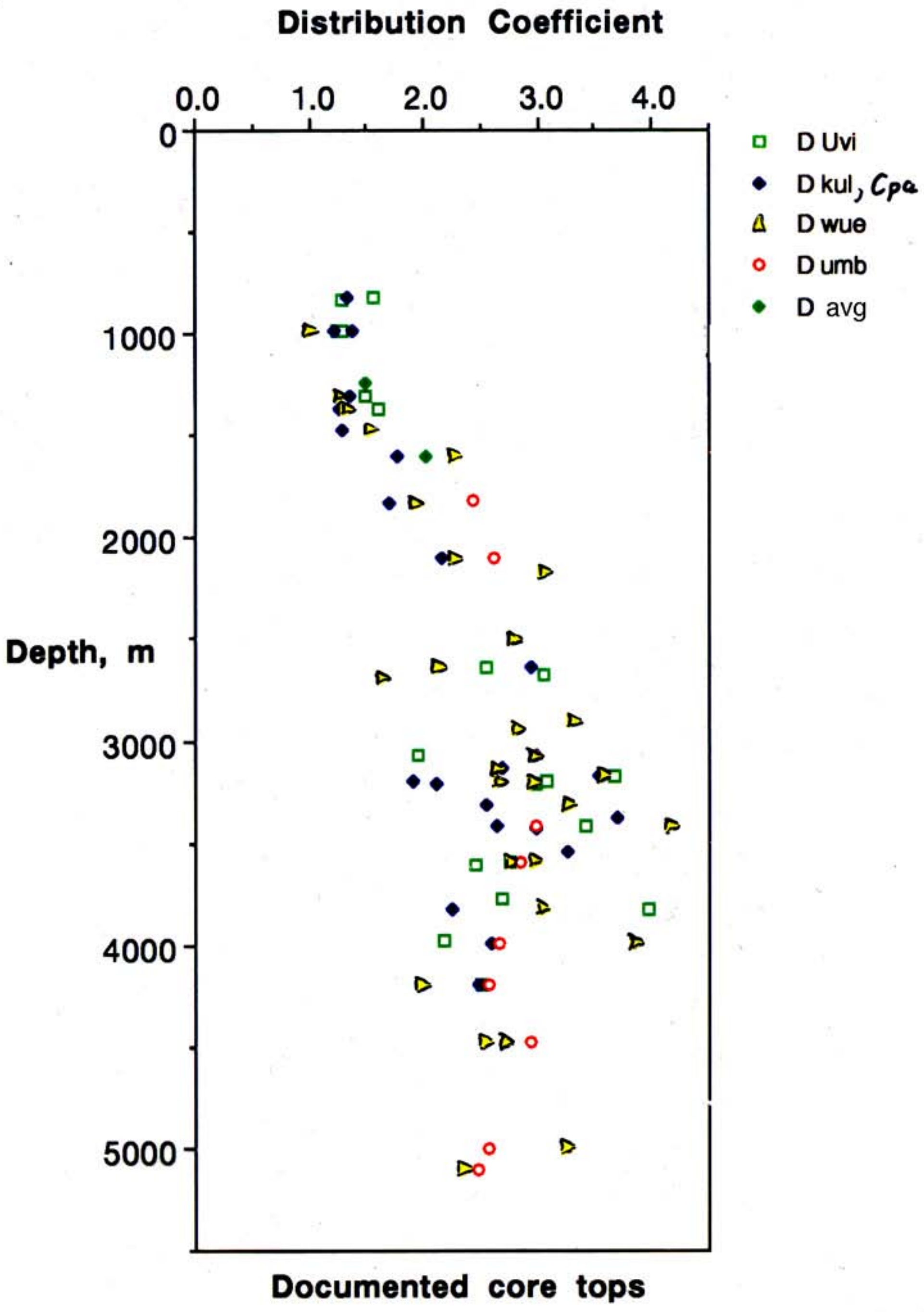
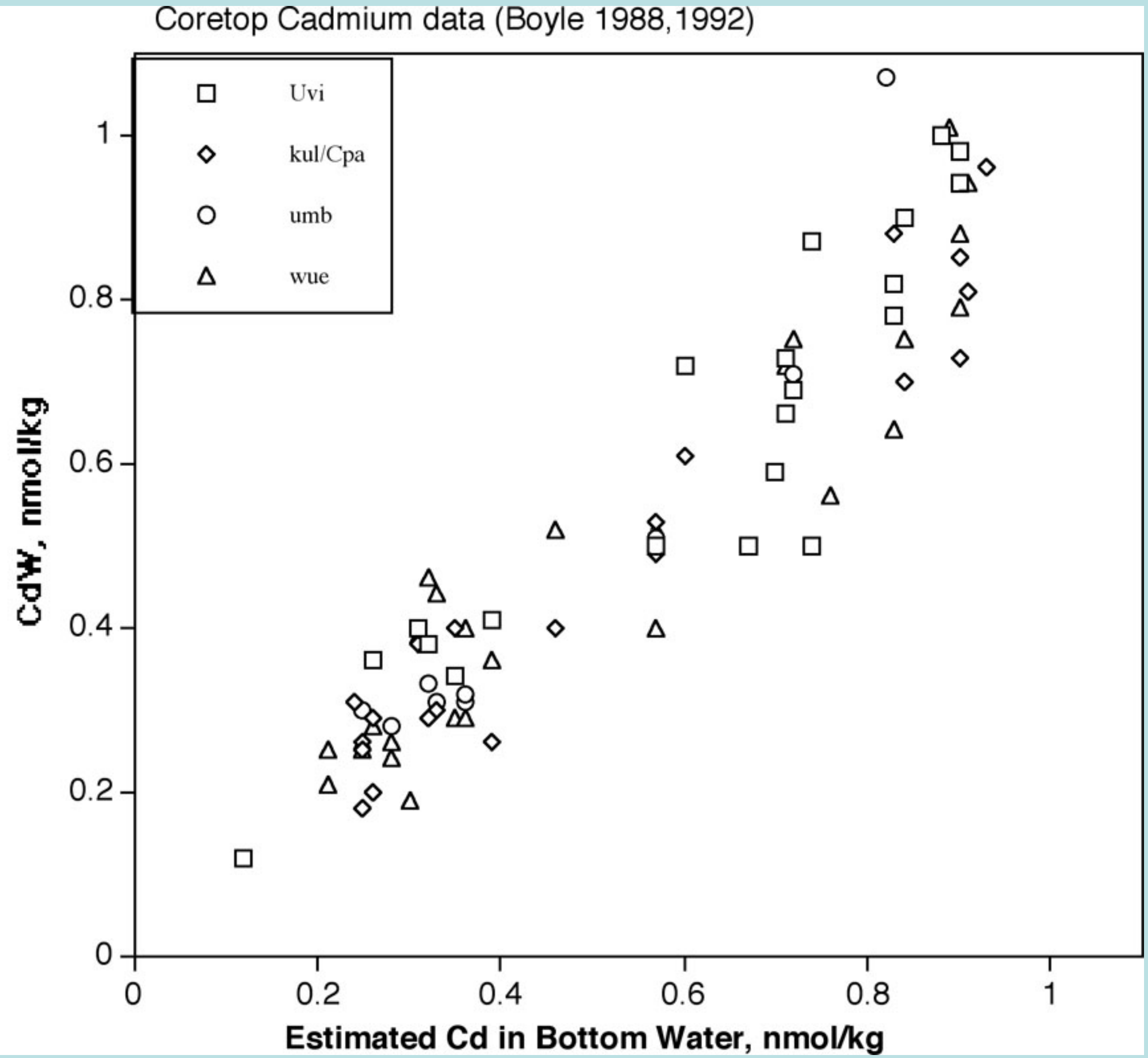
Cd/Ca in foraminifera as a tracer of ocean chemistry and circulation IV

- The main difficulty with this technique is that the cadmium content of foraminifera is very low, ranging from less than 0.01 μmol/mol for surface planktonics to 0.23 μmol/mol for Pacific benthics. Boyle (1981) demonstrated that ultrasonically-cleaned foraminifera shells contain in total 100-1000 times more cadmium than is actually contained in the lattice. This cadmium is contained in ferromanganese coatings on the surface of the shells which can be removed by a reductive cleaning treatment. In some environments, precipitation of manganese carbonate ($MnCO_3$) on the surfaces of foraminifera also leads to excessive Cd levels; it is more difficult to selective remove this phase, although acid leaching can preferentially dissolve the outer surfaces relative to the interior calcite.
- Studies by Boyle and Keigwin (1982; 1984 a,b; 1985) have shown that the $\delta^{13}C$ results from C. wuellerstorfi and Cd/Ca in several species including C. wuellerstorfi, C. kullenbergi, Uvigerina, and N. umbonifera are consistent and indicate that the nutrient content of the deep North Atlantic was about twice as high during the glacials as it is during the interglacials, which is consistent with a significant reduction in NADW, but not with cessation.
- Aragonitic *Hoeglundina* as a deep water Cd tracer.
- McCorkle, Lea et al. (1995)showed that C. wuellerstorfi from very deep Pacific cores had lower Cd than expected from bottom water chemistry
- Marchitto (2004) confirmed that there was no significant temperature effect on benthic foraminiferal Cd in the range 4°C-18°C.



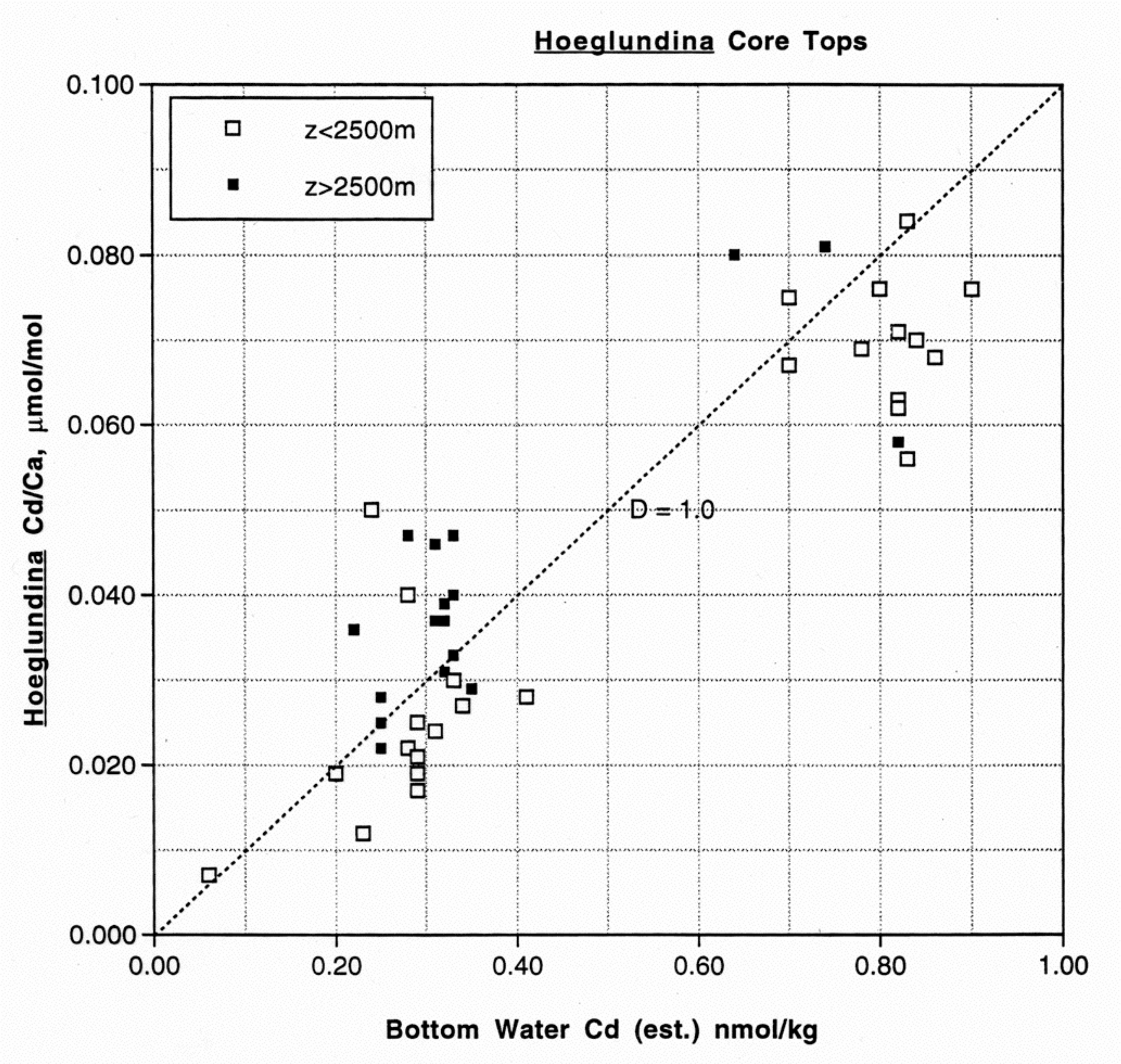
calcitic Cd/Ca partition coefficient appears to be a function of depth (Boyle, 1992)

Cd/Ca in foraminifera as a tracer of ocean chemistry and circulation III



Determination of the equilibrium partition coefficient is difficult (because of rampant disequilibrium and slow kinetics at low temperatures). And of course, organisms may choose to use their energy resources to create disequilibrium fractionations. Best course is to use empirical approach to see if the cadmium content of the foraminifera is proportional to the cadmium content of the water the organisms grown in. This has been approached by feeding radioactive cadmium to planktonic foraminifera (Delaney, Be) and by looking at the distribution of Cd in core-top benthic foraminifera relative to the bottom-water Cd content (Boyle, 1988). These studies show that the Cd content of a variety of deepwater (>2500m) calcitic foraminifera is proportional to the Cd content of the water, with $D_p \approx 2.9 \pm 0.6$. In shallower cores, the situation for Cd is more complicated. Coretop calibration shows that D changes with depth from ~1.3 at $z \leq 1100$ to D~2.9 at $z \geq 2900$ m. Boyle (1992) proposed that cadmium in the water ("CdW") should be estimated from this relationship when comparing data from depths crossing this transition. Fortunately, the aragonitic benthic foraminifera Hoeglundina elegans appears to little or no depth dependence for D (Boyle et al., 1995), which allows one to check whether the inferred depth dependence is stable. Comparison of Cd data from this species and the calcitic foraminifera indicates that the calcitic depth-dependence has remained constant between the last glacial maximum and the present.

Aragonitic *Hoeglundina* as a deep water Cd tracer



A brief history of North Atlantic Deep Water from $\delta^{13}C$ and Cd/Ca

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1983: Shackleton, Imbrie, and Hall argued that during the last glacial maximum, "the deep water of the North Atlantic Eastern Basin...was filled by a relatively cold water mass which was no richer in dissolved oxygen than deep Pacific water", based on the $\delta^{13}C$ difference between Uvigerina in cores M12392 (25°N, 16°W, 2573m) and V19-30 (3°S, 83°W, 3091m)

1985: Mix and Fairbanks make similar arguments

1983: Curry and Lohmann suggest that a large decrease in C. wuellerstorfi $\delta^{13}C$ in the deepest Eastern Atlantic Ocean the deeper parts of the eastern Atlantic basins was due to "reduced advection of O_2-rich deep water through low-latitude fracture zones, associated with increased delivery of organic matter to the deep ocean" (En 66 core suite, Sierra Leone Rise, eastern equatorial Atlantic)

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As Henry Higgins might have said:

Why can’t a foram be more like a CTD?

What do we want from foraminifera?

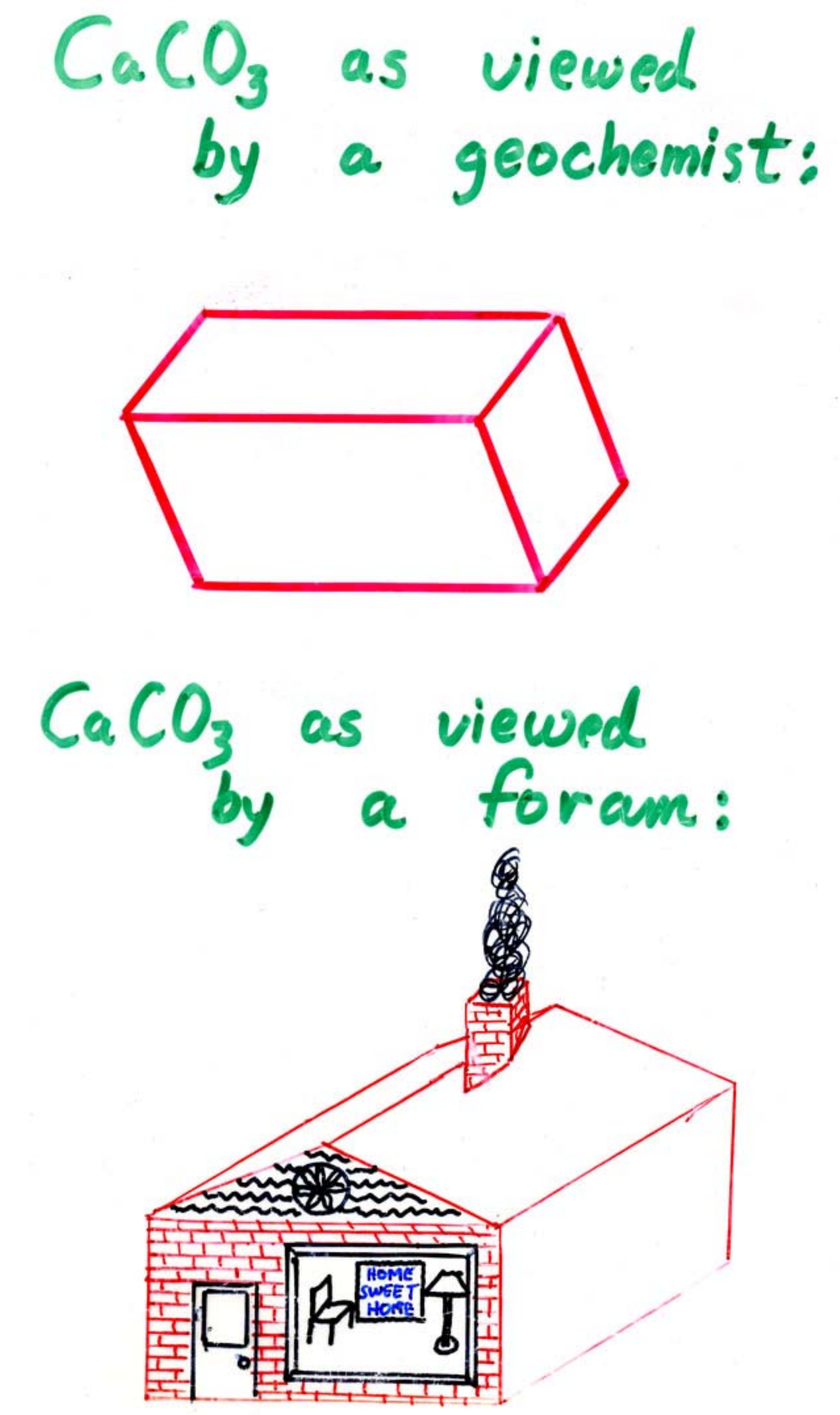
- Incorporate isotopes and minor ions at chemical equilibrium during the seconds-hours during which calcification occurs

What do we want from foraminifera?

- Incorporate isotopes and minor ions at chemical equilibrium during the seconds-hours during which calcification occurs

- Maintain those chemical properties for a hundred million years inside of a 50 µm thick shell in an environment entirely out of equilibrium with the shell properties.

Sweet home foraminifera



Review of some issues in using $\delta^{13}C$ and Cd/Ca as "paleo-nutrient indicators" in deep water paleoceanography:

Issues for both:

- infaunal habitat?
- diagenesis

$\delta^{13}C$ issues:

- species differences
- carbon flux dependence
- changes in global mean $\delta^{13}C$

Cd/Ca issues:

- cleaning
- diagenetic phases ($MnCO_3$ and CdS)
- depth-dependent D_p (calcitic species)
- undersaturation-dependent D_p

  (*C. wuellerstorfi*)

Solution:

Get a second opinion!

Foraminiferal Ba/Ca and Zn/Ca as paleoceanographic tracers

- Ba also has "nutrient-like" behavior in the ocean (lower in surface waters, higher in deep waters), but its oceanic distribution resembles that of Si or Alk more than that of P or N; this distribution is explained as due to the redissolution of the Ba-Si-Alk tracers near or on the ocean floor rather than shallower in the water column as for P, N, Cd.

- Foraminiferal Ba also has a cleaning problem; main culprit is barite ($BaSO_4$); special cleaning methods need to be employed to remove this selectively from $CaCO_3$.

- Benthic foraminiferal Ba correlates with bottom water Ba, and the three species studied give similar Ba values; it looks like Ba will be a useful paleo tracer.

- Early results of Ba studies show some similarities and some differences compared to Cd and $\delta^{13}C$.

- Foraminiferal Zn/Ca (Marchitto et al. 2000, 2002). Zn is incorporated into benthic foraminifera but the amount depends on both the Zn concentration and the carbonate ion concentration of the bottom water.

1982: Boyle and Keigwin suggest that "there has been a continuous flow of nutrient-depleted waters into the deep North Atlantic. The intensity of this source relative to nutrient-enriched southern waters diminished by about a factor of 2 during severe glaciations" - based on Cd/Ca data in CHN82-32-11PC (42°N, 32°W, 3209m) with O18 and C13 data from C. wuellerstorfi.

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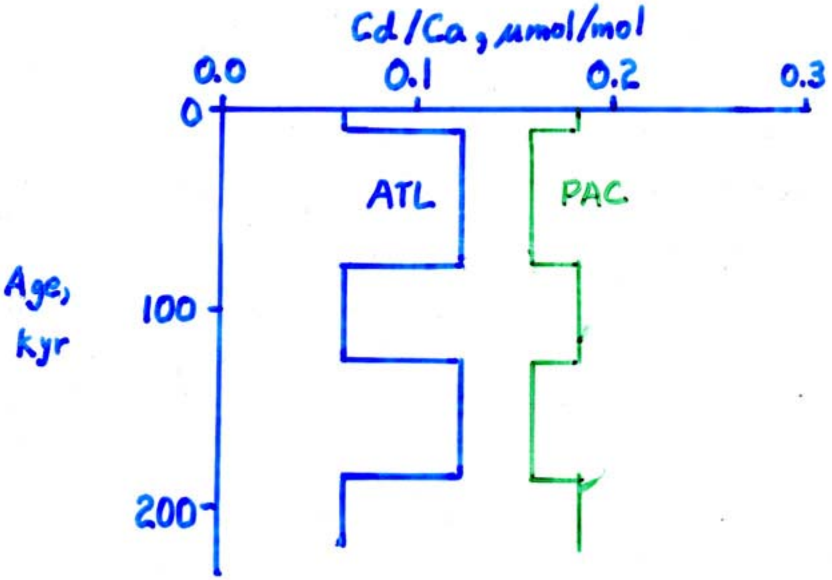
Comparison of Broecker and Peng (1984) with Boyle and Keigwin (1982) interpretations

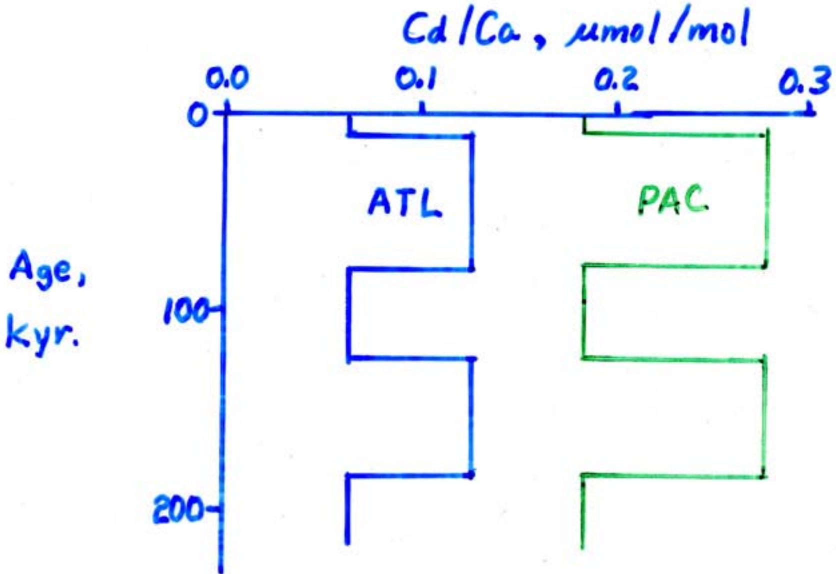
BOYLE and KEIGWIN, 1982

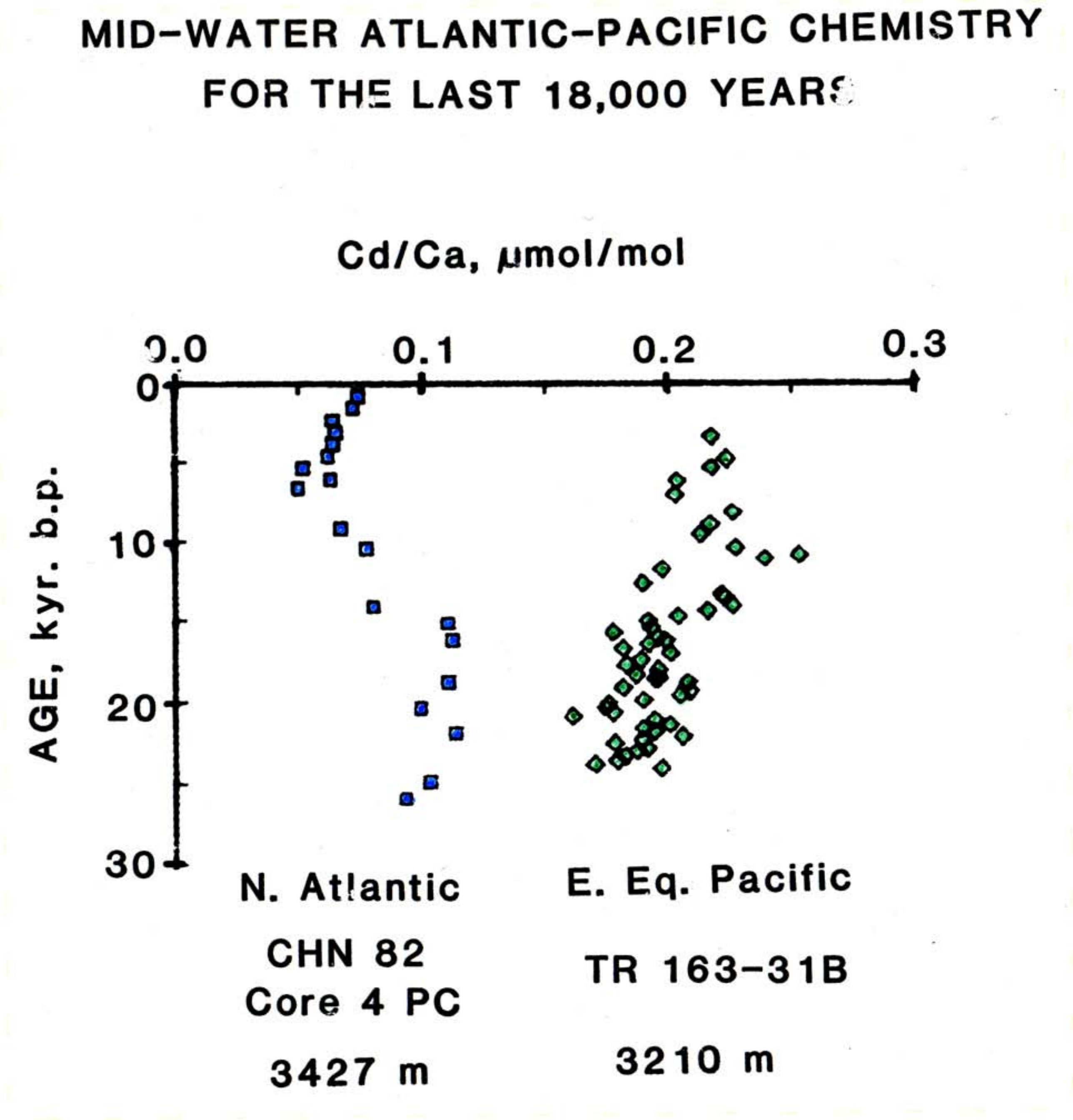
$\overline{Cd}$ = constant
circulation varies



BROECKER and PENG, 1984

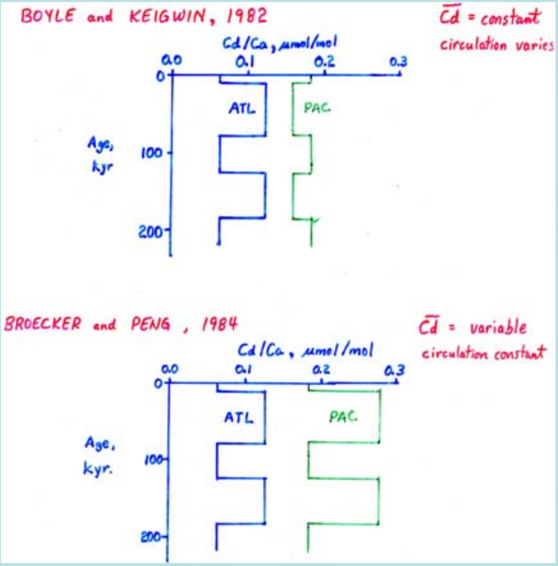
$\overline{Cd}$ = variable
circulation constant





MID-WATER ATLANTIC-PACIFIC CHEMISTRY FOR THE LAST 18,000 YEARS

Boyle and Keigwin (1986/7) Boyle (1988): show that Pacific Cd did not increase as predicted by Broecker and Peng (1984)



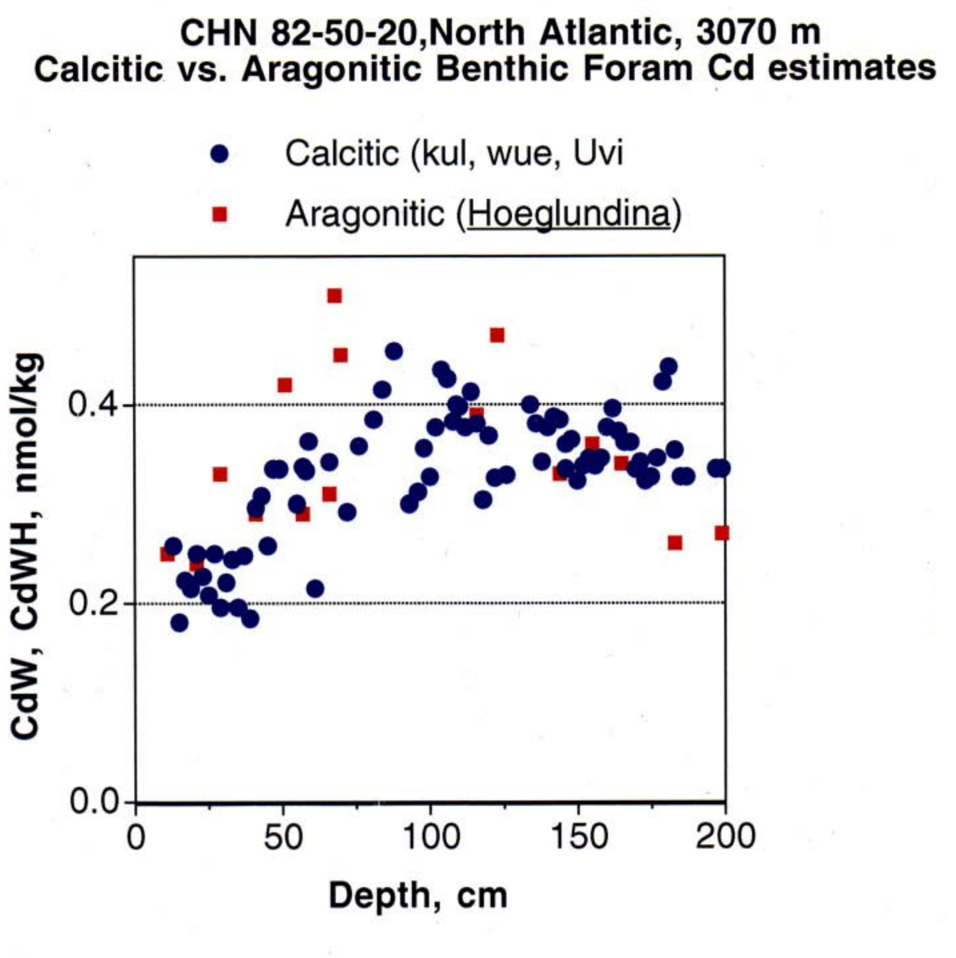
BOYLE and KEIGWIN, 1982

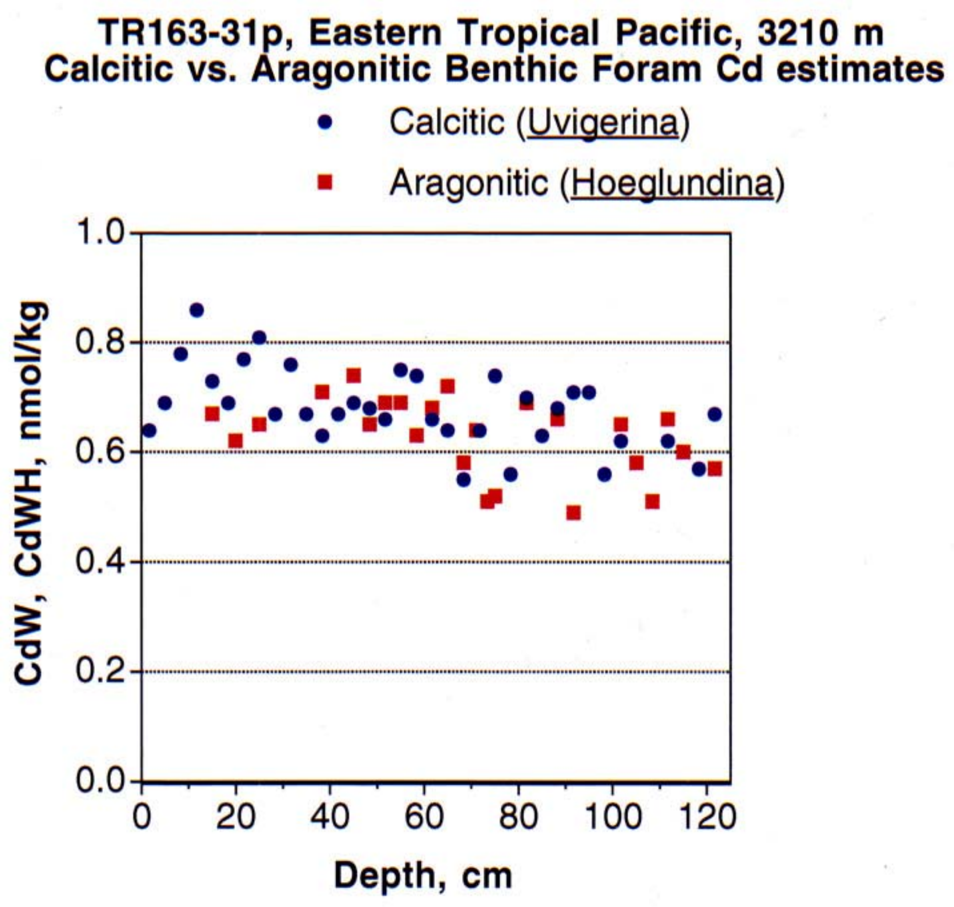
$\overline{Cd}$ = constant circulation varies

BROECKER and PENG, 1984

$\overline{Cd}$ = variable circulation constant

Comparison of Atl/Pac calcitic/aragonitic Cd data


CHN 82-50-20,North Atlantic, 3070 m
Calcitic vs. Aragonitic Benthic Foram Cd estimates


TR163-31p, Eastern Tropical Pacific, 3210 m
Calcitic vs. Aragonitic Benthic Foram Cd estimates

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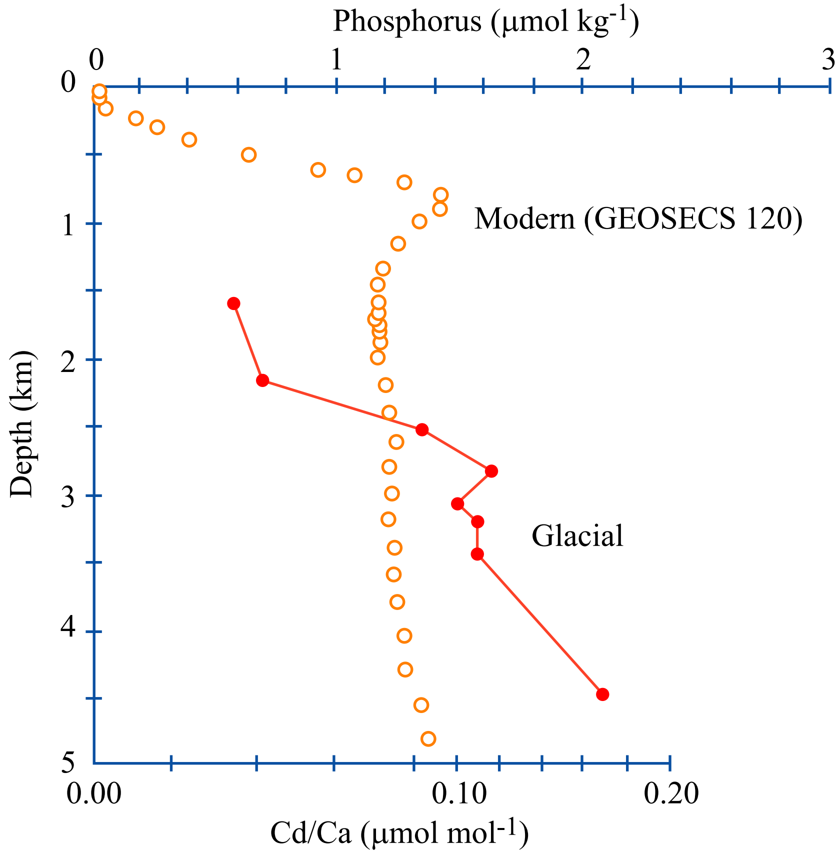
Boyle and Keigwin (1987): North Atlantic LGM nutrient profile shows reductions in upper waters, enrichments in deeper waters



Glacial depth profile of phosphorus in the modern western North Atlantic (GEOSECS station 120) compared to glacial profile.

Figure by MIT OpenCourseWare.

Boyle and Keigwin (1987): deep N. Atlantic nutrient enrichment occurred during Younger Dryas

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