12.740 Paleoceanography
Spring 2008

PALEOCEANOGRAPHY   12.740   SPRING 2006   Lecture 9

DEEP-OCEAN PALEOCEANOGRAPHY AND OCEAN CHEMISTRY: LINKS TO ATMOSPHERIC CARBON DIOXIDE and $^{14}C/^{12}C$

I. Deep water paleoceanography

  A. 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.

    1. 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.

    2. 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).

    3. 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.

    4. 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.)

    5. Few paleoceanographic interpretations based on benthic foraminifera populations have 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 <u>sign</u> was right!

Images removed due to copyright considerations.
Source: Streeter and Shackleton, 1979, figure 1 and 2.

B. Carbon isotopes as a tracer of deep ocean paleoceanography

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

        a. 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).

        b. 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.

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

    2. Because $\delta^{13}C$ is recorded in the shells of planktonic and benthic foraminifera, it is possible to determine the nutrient distribution in past oceans.

        a. Complication: $\delta^{13}C$ in forams is <u>not</u> in equilibrium or even close to it; in fact, different species have significantly different offsets from the $\delta^{13}C$ of the water.

Image removed due to copyright considerations.
Source: Duplessy et al. (1984).

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

Images removed due to copyright considerations.
Source: Zahn et al. (1987).

c. Complication: where in the sediment do foraminifera live? If they live at some depth in the sediment, δ^{13}C can be significantly different from that of the bottom water.

d. Complication: The <u>average</u> δ^{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 <u>local</u> downcore records of δ^{13}C have a large (and often dominant) component due to changes in the ocean average δ^{13}C, and it is necessary to somehow correct for this in determining the spatial δ^{13}C distribution at a given time.

3. Because of these complications, early δ^{13}C studies of benthic foraminifera have been characterized by "incomplete interpretations" which were modified later. For example, Shackleton (1977) attributed the C-13 changes from <u>Uvigerina</u> off Northwestern Africa (core M12392) (almost) solely to changes in the global oceanic δ^{13}C due to a diminished LGM soil/biospheric carbon reservoir.

Image removed due to copyright considerations.
Source: Shackleton (1977), in Fate of Fossil Fuel CO2, figure 3.

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 <u>Uvigerina</u> 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 <u>difference</u>

between Atlantic and Pacific records to NADW fluctuations (which would have therefore been a large portion of the total $\delta^{13}C$ record in the Atlantic core. Zahn et al. (1986) showed that Uvigerina shows variable $\delta^{13}C$ 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 $\delta^{13}C$ offsets for Uvigerina. Hence the role of NADW fluctuations was smaller than it appeared in the 1983 paper.

Images removed due to copyright considerations.
Source: Shackleton, Imbrie, and Hall (1983), figure 2, 3, and 5.

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

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

1. 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.

Image removed due to copyright considerations.
Source: Boyle (1994).

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

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

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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
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For an <u>ideal</u> 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).

3. 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 <u>partition coefficient</u>

4. 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≤1100 to D~2.9 at z≥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 <u>Hoeglundina elegans</u> 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.

Image removed due to copyright considerations.
Source: Boyle, 1992.

5. 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.

6. 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.

7. Aragonitic Hoeglundina as a deep water Cd tracer.

8. McCorkle, Lea et al. (1995)showed that C. wuellerstorfi from very deep Pacific cores had lower Cd than expected from bottom water chemistry

9. Marchitto (2004) confirmed that there was no significant temperature effect on benthic foraminiferal Cd in the range 4°C-18°C.

D. Paired $\delta^{13}C$ and Cd/Ca data as tracers of ocean circulation and chemistry.

1. Even if both tracers contained exactly the same information, the combination of both (each with different own artifacts and problems) can make for a more convincing case when they both agree.

2. Although both $\delta^{13}C$ and Cd plot linearly against P (and hence contain similar information on oceanic chemical fractionation due to deep ocean circulation patters), paired data on both tracers provides more information because the slope of paired isochronous data provides information on the Cd:P ratio of the ocean and the intercept provides information on the P content of the ocean. (Boyle, 1985).

3. "$\delta^{13}C_{as}$" concept (Lynch-Stieglitz et al., 1995): the role of gas exchange in influencing oceanic $\delta^{13}C$. At equilibrium, the d13C of seawater in equilibrium with the atmosphere is a function of the temperature:

Temperature-dependent equilibrium: fixing the carbon isotope composition of the atmosphere and allowing seawater to equilibrate:

	25°C	0°C
gaseous CO_2	-6.4	-6.4
~~		
aqueous CO_2	-7.6	-7.7
HCO_3^-	+1.5	+4.4
$CO_3^=$	-0.5	+0.8
$(CaCO_3)$	+3.0	+0.0
$\overline{TCO_2}$	+1.3	+4.1

Because of this temperature-dependent isotopic fractionation, gas exchange tends to make higher latitude waters heavier in $\delta^{13}C$ (and lower latitude waters lighter). This gas exchange process does not affect phosphorus or cadmium, and hence is a potential mechanism for making the oceanic $\delta^{13}C$ distribution different from that of P or Cd.

Lynch-Stieglitz et al., 1995 proposed that the "preformed" $\delta^{13}C$ distribution could be estimated by correcting benthic $\delta^{13}C$ for deep respiration using benthic Cd/Ca data and assuming a Cd:C "Redfield Ratio". For this method to work, both tracers must be free of artifacts, and at the present time this cannot be guaranteed.

E. Foraminiferal Ba/Ca as a paleoceanographic tracer

1. 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 <u>near or on the ocean floor</u> rather than shallower in the water column as for P, N, Cd.

2. 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 $CaCO_3$.

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.

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

F. 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.

G. Results from deep-water paleochemistry studies

1. North Atlantic <u>Deep</u> Water flow was diminished, but did not cease (at least on time scales approachable for 3 cm/kyr sediment cores). Evidence: Cd in several benthic species and $\delta^{13}C$ in <u>C. wuellerstorfi</u> show that NADW remains nutrient-depleted relative to Pacific Deep Water (Boyle and Keigwin, 1982; 1985/6).

2. Intermediate-depth water in the North Atlantic ocean was more depleted in nutrients than at present. Evidence: Cd and $\delta^{13}C$ in Caribbean Sea benthic forams; continental margin cores (East and Western margins); little change in nutrients at 2100m on Mid-Atlantic Ridge (in contrast to deeper increase) (Boyle and Keigwin, 1987).

3. Curry and Lohmann (1983) study of bathymetric gradients in $\delta^{13}C$ in the eastern equatorial Atlantic.

4. Duplessy et al. (1988) and Curry et al. (1988) studies of Atlantic and global deepwater $\delta^{13}C$ distributions during the last 18,000 years.

5. Kallel et al. (1988) study of northern Indian ocean shallow cores. Boyle et al. (1992) amplification using Cd in aragonitic and calcitic benthics.

6. Other basins: the jury is still out. Some special interest in the North Pacific, since some people have wondered if deepwater might have formed there during glacial times.

II. ^{14}C as a deep-water and ventilation rate tracer

A. The basic idea is simple: benthic and planktonic foraminifera incorporate ^{14}C into their shells and hence represent deep and surface water ^{14}C. Since ^{14}C decreases as a water mass "ages", the contrast between surface and deep waters can be used as a circulation tracer. Coexisting pairs of benthic and planktonic foraminifera from sediment cores allows us to do this in the past, in principle.

B. In practice, there are some major obstacles to this idea. The most serious are mixing, statistics, and dissolution. Because a range of ages is represented by specimens, one must collect enough to compensate for the sampling statistics; this problem is more serious than for chemical tracers (because ^{14}C always changes by a factor of two every 5730 years, while Cd or $\delta^{18}O$ may not). Furthermore, changes in P/B abundance patterns and differential dissolution can create artifacts. We also need to understand something more about the behavior of ^{14}C on the surface of the earth. But working with deep sea corals (no bioturbation) or planktonic-benthic pairs from abundance maxima (hence minimizing the effects of bioturbation, this method leads to some very interesting results (Keigwin and Schlegel, 2002; Robinson et al., 2005).

Image removed due to copyright considerations.
Source: Duplessy et al. (1988).

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Please see:
Figure 8 in Keigwin and Schlegel. "Ventilation in the Western North Atlantic." Paleoc 19 (2004): 4012.

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Figure 3 in Robinson L. F., J. F. Adkins, L. D. Keigwin, J. Southon, D. P. Fernandez, S. L. Wang, and D. S. Scheirer. "Variability in the Western North Atlantic During the Last Deglaciation." Science 310 (2005): 1469-1473.

III. ^{231}Pa/^{230}Th as a tracer of deep ocean ventilation rates (Yu et al.,1996; Marchal et al.,2000; McManus et al. 2004). These isotopes are generated from the decay of ^{235}U and ^{234}U at a precisely known rate that is uniform throughout the ocean. But ^{230}Th is more "particle reactive than ^{231}Pa (deep sea Th residence time is ~30 years whereas the Pa residence time is ~150 years). Hence ocean currents such as NADW can transport ^{231}Pa away from their origin to regions where the particle flux (and scavenging) is higher. The sediments of the modern North Atlantic are depleted in ^{231}Pa/^{230}Th as a result of this deep water transport of ^{231}Pa out of the basin. Yu et al. (1996) found that the LGM Atlantic was similarly depleted, hence they argued that there must have been a net flow of NADW out of the basin comparable to the modern rate. Subsequent model studies (Marchal et al., 2000) have shown that the constraint is probably a $\pm$50% estimate (i.e., NADW export from the Atlantic could have been as low as 50% of the present value, or 50% higher).

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Please see:
Yu, E. -F., R. Francois, and M. P. Bacon. "Similar rates of modern and last-glacial ocean thermohaline circulation inferred from radiochemical data." *Nature* 379 (1996): 689-694.

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