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Redfield ratios of remineralization determined by nutrient data analysis

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Abstract. A nonlinear inverse method is applied to nutrient data upon approximately 20 neutral surfaces in each of the South Atlantic, Indian, and Pacific basins, between 400 and 4000 m depth. By accounting for the gradients in nutrients due to the mixing of "preformed" concentrations of the major water masses, the nutrient changes due to biological activity are examined, and the time-mean, basin-wide Redfield ratios calculated. It is found that the $P/N/C_{org}/-O_2$ ratios of nutrient regeneration between 400 and 4000 m (corrected for the effect of denitrification) are approximately constant with depth and basin, at a value of 1/16±1/117±14/170±10. These ratios agree with those of fresh organic matter, suggesting that the flux of organic material to the deep ocean may be dominated by fast-sinking matter produced by sporadic, high-productivity events. Sedimentary denitrification reduces the N/P utilization ratio to 12 ± 2 between 1000 and 3000 m. In the Indian and Pacific basins the C_{org}/C_{inorg} regeneration ratio decreases from approximately 7 ± 3 at 400 m to 3 ± 1 at 1000 m and to 1 ± 0.5 at 4000 m, suggesting a significant amount of calcium carbonate dissolution above the calcite lysoclines in the Indian and Pacific oceans.

1. Introduction

The utilization of primary nutrients by marine organisms during the synthesis and subsequent remineralization of organic matter is often represented by the equation

$$H_3PO_4 + \alpha\, HNO_3 + \beta\, CO_2 + \lambda\, H_2O = C_\beta H_\zeta O_\varphi N_\alpha P + \gamma\, O_2 \quad (1)$$

where the balance coefficients α, β, and γ have generally become known as the "Redfield" ratios, in honor of A. C. Redfield, who was among the first to take steps in quantifying these ratios and explaining their importance in global biogeochemistry. Redfield ratios are particularly useful in oceanography in estimating the utilization of one nutrient from another (e.g., carbon new production from nitrate supply to the euphotic zone), and in deriving dynamically passive conservative tracers (e.g., "NO" and "PO" [*Broecker*, 1974; *Broecker et al.*, 1985]).

The "traditional" $P/N/C_{org}$ Redfield ratios, of *Redfield et al.* [1963], are 1/16/106, based on planktonic decomposition studies [*Fleming*, 1940]; an $-O_2/P$ ratio of 138 was inferred by effectively assuming an organic matter stoichiometric composition of $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$ in (1) and balancing the equation. However, recent studies have put these traditional values into question. *Takahashi et al.* [1985], examining correlated changes in nutrients on isopycnals in the thermocline, concluded that the actual $-O_2/P$ ratio there was at a higher value of 172; again assuming an organic matter stoichiometry of $(CH_2O)_x(NH_3)_{16}H_3PO_4$ would then suggest a C_{org}/P ratio of 140.

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Broecker et al. [1985] and *Peng and Broecker* [1987] extended this finding by asserting that the $-O_2/P$ ratio was near 175 not only in the thermocline, but at all depths throughout the entire world ocean. In conflict with this, *Minster and Boulahdid* [1987] and *Boulahdid and Minster* [1989], using the same data, suggested that rather it was the $-O_2/N$ ratio that was constant with depth, at a value of 9, and that in fact the $-O_2/P$ ratio, while near 172 in the thermocline, decreased with depth to approximately 115 in all oceans. Finally, the open ocean sediment trap studies of *Martin et al.* [1987] have suggested the opposite viewpoint, that is, that the $N/C_{org}/-O_2$ regeneration ratios increase from 16/99/163 at 100 m depth to 16/164/259 at 5000 m depth. (Assuming from sediment trap studies that the N/P ratio is 16 or greater, this would suggest an $-O_2/P$ ratio of 259 or greater.)

As each study contradicted a previous one, the question of whether the Redfield ratios are constant, decrease, or increase with depth, and to what degree, we felt was still unresolved. In addition, we noted that each study contained certain weaknesse that put their results into question. Here will be described method we believe to be a significant improvement over th previous techniques.

2. The Technique

While the elementary composition of planktonic matter can estimated, it does not necessarily equal the ratio in wh nutrients are added to seawater during remineralization, beca certain elements may be preferentially remineralized with de For this reason the traditional Redfield ratios are not necess applicable at depth. Furthermore, the observed vertical flu organic matter below 400 m has a very small vertical grac such that the water column nutrient utilization ratios cann

accurately estimated from these measurements, which requires taking derivatives and calculating quotients from the fluxes. (It is for this reason that the estimates of *Martin et al.* [1987] below 400 m are likely inaccurate—they are based on small vertical flux gradients.) Redfield ratios of nutrient utilization can also be determined by looking at temporal changes in nutrient concentrations; however, this type of analysis is limited to times and places that undergo significant temporal changes in nutrients. Finally, Redfield ratios can be determined by examining spatial changes in nutrient concentrations. This method is advantageous in that thc large-scale nutrient gradients intrinsically involve averages over time and space, and can be used to examined the deep ocean Redfield ratios, over which there is present disagreement. As such, this last method is the one that will be followed here.

Consider the advection of a single water mass in the deep ocean. As remineralization occurs within the water mass, its nutrient concentrations should increase, causing a spatial gradient in nutrient concentrations. In such a case the Redfield ratios can be determined by simply examining the correlations between nutrients in these spatial gradients. When two water masses are mixing, the situation is slightly more complicated; one needs to account for that part of the nutrient gradient that is due to the mixing of the initial nutrient concentrations of the water masses. (A hypothetical two end-member system and an example of a real, approximately two end-member system are shown in Figure 1.) This can be expressed mathematically as follows.

Let us consider a horizontal domain on which two "end-member" water masses are mixing, the first end-member having properties $\theta_1, P_1, N_1, O_1, C_1$, and A_1, and the second $\theta_2, P_2, N_2, O_2, C_2$, and A_2 where θ stands for potential temperature, P for phosphate, N for nitrate, O for molecular oxygen, C for total dissolved inorganic carbon, and A for alkalinity. At a given intermediate location (observation i) on the surface, this allows us to write the following:

$$
\begin{aligned}
1 &= f_1^i + f_2^i \\
\theta_{obs}^i &= f_1^i \theta_1 + f_2^i \theta_2 \\
P_{obs}^i &= f_1^i P_1 + f_2^i P_2 + \Delta P^i \\
N_{obs}^i &= f_1^i N_1 + f_2^i N_2 + r_{N/P}\, \Delta P^i \\
O_{obs}^i &= f_1^i O_1 + f_2^i O_2 - r_{-O_2/P}\, \Delta P^i \\
C_{obs}^i &= f_1^i C_1 + f_2^i C_2 + r_{C/P}\, \Delta P^i + \Delta C_{inorg}^i \\
A_{obs}^i &= f_1^i A_1 + f_2^i A_2 - r_{N/P}\, \Delta P^i + 2\, \Delta C_{inorg}^i
\end{aligned}
$$

where subscript obs stands for an observation, 1 for first end-member, 2 for second end-member; f stands for end-member fraction, ΔP for the phosphate added from remineralization of organic material, ΔC_{inorg} for the carbon added from the dissolution of calcareous material, and $r_{N/P}$, $r_{-O_2/P}$, and $r_{C/P}$ stand for the nitrate/phosphate, oxygen/phosphate, and organic carbon/phosphate Redfield ratios, respectively.

These equations indicate that at observation i the potential temperature will be a linear combination of that of the end-members, where the fractional contributions add to one. The same is true for the nutrient concentrations, plus whatever amount that may have been added by remineralization. Redfield ratios are used to relate the amount of remineralized phosphate to the remineralized amounts of the other nutrients; also note that oxygen is removed during remineralization (thus a negative sign), total carbon has an additional amount added from $CaCO_3$ dissolution, and alkalinity is altered by changes in NO_3^- and Ca^{2+} concentrations.

Each observation made in a given two end-member mixing domain would yield a set of the above equations. Therefore if K stations sampled the domain, one would have 7 K equations, and

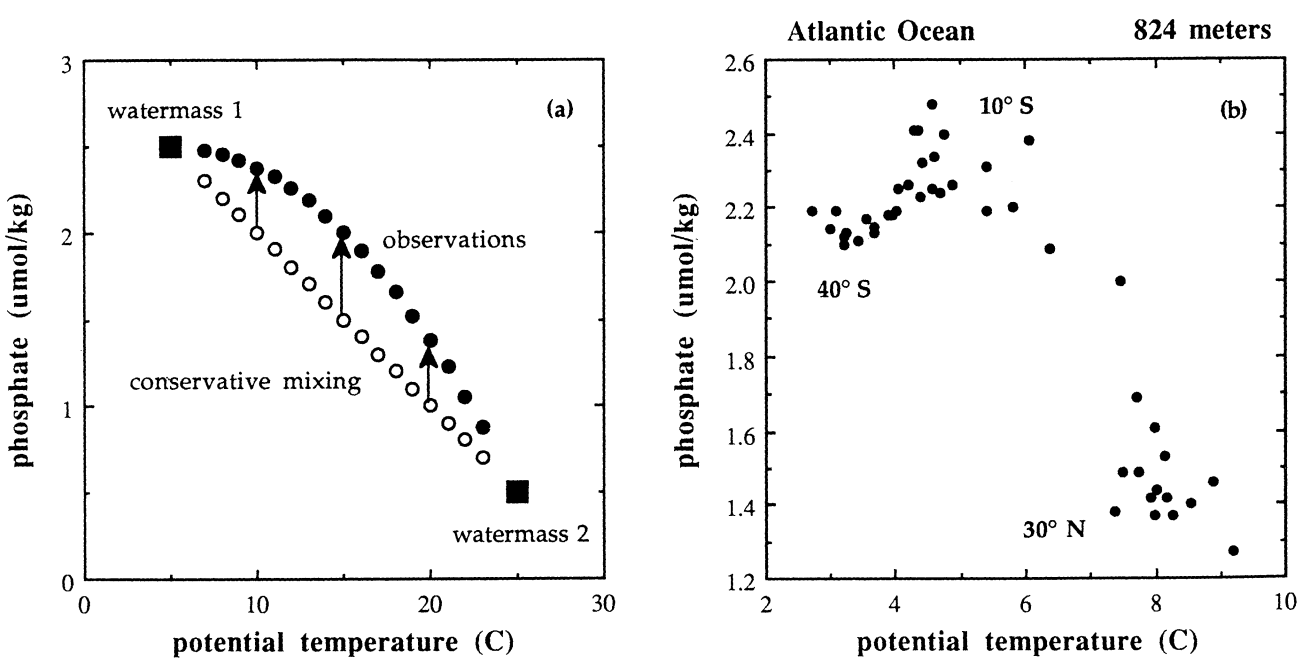

Figure 1. (a) Phosphate versus potential temperature in a hypothetical two end-member mixing system. Remineralizaton in the interior causes a "bow" from the conservative mixing line between end-member water masses, in the direction of increased phosphate. (b) GEOSECS Atlantic Ocean data interpolated onto a neutral surface that intersects station 42 at 824 m. Labels indicate the locations of the observations. Note that no known water mass enters the Atlantic at 10°S; the phosphate maximum is due to remineralization off of Africa.

4 K +15 unknowns (f_1^i, f_2^i, ΔP^i, and ΔC_{inorg}^i being different at each station, and the end-member concentrations and Redfield ratios assumed to be constant over the entire domain). Therefore if K > 5, the system would be potentially overdetermined, and all the variables on the right side of the equations, including the Redfield ratios, could be determined.

However, if the model is overcomplicated (namely if it contains more terms than can be independently determined by the data), certain terms may be underdetermined. As it turned out in practice, the ΔC_{inorg}^i terms in the above set of equations were found to be insufficiently defined. This may in part be due to the fact that the observed GEOSECS alkalinity and total carbon gradients are very small in the deep ocean relative to their measurement errors, making the calcium carbonate signal difficult to extract. The substitution $\Delta C_{inorg}^i = r_{I/P}\,\Delta P^i$, with $r_{I/P}$ constant over the entire surface, was therefore used to reduce the number of unknowns (where $r_{I/P}$ is the average ratio of particulate inorganic carbon dissolution to phosphate regeneration). This is actually not a good approximation, as one would expect $r_{I/P}$ to vary with latitude. However, making this approximation overdetermines the otherwise underdetermined parts of system, such that more reasonable estimates, with less scatter and smaller associated uncertainties, are obtained than when keeping the model more complicated.

The system of equations used in practice to determine the Redfield ratios was therefore

$$\theta_{obs}^i = f_1^i(\theta_1 - \theta_2) + \theta_2 \quad (2a)$$
$$P_{obs}^i = f_1^i(P_1 - P_2) + P_2 + \Delta P^i \quad (2b)$$
$$N_{obs}^i = f_1^i(N_1 - N_2) + N_2 + r_{N/P}\,\Delta P^i \quad (2c)$$
$$O_{obs}^i = f_1^i(O_1 - O_2) + O_2 - r_{-O_2/P}\,\Delta P^i \quad (2d)$$
$$C_{obs}^i = f_1^i(C_1 - C_2) + C_2 + (r_{I/P} + r_{C/P})\,\Delta P^i \quad (2e)$$
$$A_{obs}^i = f_1^i(A_1 - A_2) + A_2 + (2\,r_{I/P} - r_{N/P})\,\Delta P^i \quad (2f)$$

where the substitution $f_2^i = 1 - f_1^i$ was used, in order to bring the left hand side of the equations to all observable quantities. These equations are basically the same as those used by *Minster and Boulahdid* [1987].

In situations where it appeared remineralization was occurring within a single water mass (as evidenced by lack of change in potential temperature), a one end-member model was used:

$$P_{obs}^i = P_1 + \Delta P^i$$
$$N_{obs}^i = N_1 + r_{N/P}\,\Delta P^i$$
$$O_{obs}^i = O_1 - r_{-O_2/P}\,\Delta P^i$$
$$C_{obs}^i = C_1 + (r_{I/P} + r_{C/P})\,\Delta P^i$$
$$A_{obs}^i = A_1 + (2\,r_{I/P} - r_{N/P})\,\Delta P^i$$

A three end-member model was also formulated but always appeared to be underdetermined under this technique. Therefore three-or-more water mass mixing regions were avoided.

In addition, a model including denitrification was employed in some of the scenarios on certain levels in the Indian Ocean where denitrification is apparent at particular stations (namely GEOSECS stations 409-420 in the Arabian Sea):

$$\theta_{obs}^i = f_1^i(\theta_1 - \theta_2) + \theta_2$$
$$P_{obs}^i = f_1^i(P_1 - P_2) + P_2 + \Delta P^i + r_D\,\Delta N^i$$
$$N_{obs}^i = f_1^i(N_1 - N_2) + N_2 + r_{N/P}\,\Delta P^i - \Delta N^i$$
$$O_{obs}^i = f_1^i(O_1 - O_2) + O_2 - r_{-O_2/P}\,\Delta P^i$$
$$C_{obs}^i = f_1^i(C_1 - C_2) + C_2 + r_{I/P} + r_{C/P})\,\Delta P^i + r_{C/P}\,r_D\,\Delta N^i$$
$$A_{obs}^i = f_1^i(A_1 - A_2) + A_2 + (2\,r_{I/P} - r_{N/P})\,\Delta P^i + \Delta N^i$$

In this model ΔN^i is the amount of nitrate removed by denitrification, and r_D is the ratio of phosphorus remineralized for a given loss of nitrate (taken as 0.0103 ± 0.0027, based on stoichiometric relationships).

GEOSECS nutrient data [*Bainbridge*, 1981a; *Broecker et al.*, 1982; *Weiss et al.*, 1983] were used in this study, not only on account of their global coverage but also because they are the data that spurred the recent controversy (i.e., between *Broecker et al.* [1985] and *Minster and Boulahdid* [1987]). The following offsets were applied:

stations 28-34: $\Sigma CO_2^{measured}$ - 17	[*Bainbridge*, 1981b, p. 2]
corrections to Pacific ΣCO_2 and ALK	[*Craig et al.*, 1981, p. 2]
stations 201-454: $\Sigma CO_2^{measured}$ - 15	[*Takahashi*, 1983, p. 5]
various corrections to PO_4	[*Broecker et al.*, 1985]

The titrimetric ΣCO_2 data were used. Neither total carbon nor alkalinity were normalized to salinity, as it would be inappropriate in the context of the model, which accounts for preformed nutrient concentrations explicitly.

The data were linearly interpolated from station cast data to neutral surfaces, upon which water masses preferentially move and mix [*McDougall*, 1987a]. This was done using the subroutine APPRNS by T. McDougall. Over 14 levels were examined in each of the South Atlantic, Indian, and south central Pacific oceans, with mean depths ranging between 400 and 4000 m. The South Atlantic Ocean (~ 20°N to ~ 50°S) was a two end-member domain at all depths between 400 and 4000 m, with a northern component (which is a combination of NADW and Mediterranean Sea Water, varying with depth) mixing with a southern component (AAIW, AACW, or AABW, depending on depth). The Indian Ocean (20°N to 30°S) was found to be two end-member between 400 and approximately 2000 m (a southern component mixing with Arabian Sea Water), and one end-member below 2000 m (southern component only). The south central Pacific domain (between 10°N and 30°S) was one end-member at all depths below 400 m, as suggested by constancy in potential temperature on neutral surfaces.

The North Atlantic was avoided, as it involved three or more end-member mixing. The North Pacific thermocline was also not analyzed, as it contained unreliable data (namely leg 1 [*Broecker et al.*, 1985]), three end-member mixing, and denitrification. The southern ocean contained too few stations and insufficient latera nutrient gradients. Analysis was also not conducted shallowe than approximately 350 m in each ocean, as the situation becam too complex for a realistic application of this model (e.g., mor than two end-members, temporal variability in end-membe nutrient concentrations, and possibly significant dianeutr fluxes) in addition to inaccurate GEOSECS ΣCO_2 data above 5(m (T. Takahashi, personal communication, 1989) and t presence of anthropogenic carbon. (While the number of er members in a particular situation could perhaps be decreased reducing the domain size, this would result in reduced horizor

gradients and therefore a reduced signal, and too few stations to overdetermine the equations.)

The main advantage of this technique over that of *Takahashi et al.* [1985] is that all parameters can be solved for simultaneously, rather than having to make questionable apriori estimates of the end-member nutrient properties, which strongly influence subsequent estimates of the Redfield ratios. (In particular, examination of the nutrient data suggests that the preformed nutrient concentrations of deep water masses are in part the product of significant subsurface water mass mixing, such that extrapolating nutrients to sea surface conditions may simply be incorrect.) The main advantage of this technique over that of *Minster and Boulahdid* [1987] and *Boulahdid and Minster* [1989] is the use of neutral surfaces rather than sigma theta surfaces (which are poor representatives of water mass trajectories in the deep ocean); in addition, on several occasions they employed a three end-member mixing model in which an $r_{-O_2/N}$ of 9 was automatically assumed, which influenced their calculations on these surfaces [*Minster and Boulahdid*, 1987, p. 1999].

Other advantages of our technique are the following:

1. The whole suite of primary nutrients ($P/N/-O_2/C_{org}/C_{inorg}$) is examined, and examined simultaneously, which is important so that the problem can be fully and consistently constrained. It was often found that each nutrient constrained the solution (namely the end-member properties) in a unique way, such that inconsistencies could arise if the nutrient relationships were only examined one at a time [e.g., *Broecker et al.*, 1985].

2. We have analyzed more surfaces than all the other studies added together. In addition to providing an ideal vertical resolution with a single technique, this was also found to be important for verification of the results at each particular depth.

3. As opposed to the linear regression techniques [*Broecker et al.*, 1985; *Peng and Broecker*, 1987], end-member properties, mixing fractions, and remineralization terms were all calculated and could be observed to make sure that they were realistic (e.g., non-negative).

4. Our model also appropriately accounted for the influence of denitrification in the Indian Ocean thermocline (through use of a denitrification term), which the other methods did not.

The primary disadvantage associated with this technique is its sensitivity to the set of observations chosen for analysis (particularly those at the extremes in potential temperature, which heavily influence the "best fit" to the end-member mixing trend). That is, as our method derives all parameters from the information in the data, rather than apriori assumptions, this technique is probably more sensitive to the choice of data than previous studies. Every effort has been made to explore this sensitivity however by varying the stations used in many possible combinations, such that any bias due to station choice hopefully has been successfully avoided. In a sense, the sensitivity to data choice in this method has replaced the sensitivity to apriori end-member choice of previous methods, such that our method can be thought of as putting the sensitivity where it belongs—with the data, rather than apriori assumptions.

3. Solving the Equations

The generalized, nonlinear inverse ("least squares") technique of *Tarantola and Valette* [1982] was used to fit the equations to the observations. A main advantage of their technique is that even underdetermined or partially determined systems of equations can be approached. In their technique, initial guesses are required for all parameters, as well as standard deviations of confidence in these guesses.

On a given surface, observations were used that fell within the particular one or two end-member domain under analysis. (Data on apparent seasonal outcrops were eliminated from consideration.) The following measurement errors were assigned to the data: potential temperature, 0.005 °C; phosphate, 0.01 μM/kg; nitrate, 0.1 μM/kg; oxygen, 1 μM/kg; total carbon, 11 μM/kg; alkalinity, 8 μEq/kg. The phosphate, nitrate and oxygen errors were based on the mean standard deviations of replicate rosette samples (on single casts). The potential temperature error was based on thermometer precision as reported by *Weiss et al.* [1983, p. 2] and the total carbon and alkalinity errors were those suggested by *Takahashi* [1983, p. 7].

In order to make end-member initial guesses systematically, an atlas of 1° × 1° resolution on each surface was interpolated from the station data. (The interpolation was conducted by weighting observations relative to their distance from the point in question; see *Anderson* [1993].) A temperature range for each end-member was chosen, and the atlas searched to find the range of nutrient concentrations coinciding with these temperatures. In this way the end-member guesses were determined. Initial guesses for f_1^i were based upon (2a), θ_{obs}^i, and the guesses for θ_1 and θ_2. The confidences in θ_1 and θ_2 were propagated to find the confidence in f_1^i. Similarly, guesses for ΔP^i were based on (2b), P_{obs}^i, and the guesses for f_1^i, P_1 and P_2, with errors again propagated to estimate the confidence.

The standard guess for $r_{N/P}$ was 16 ± 2; the error was expanded (e.g., to ± 6) whenever the result pushed close to the limits. Guesses for $r_{-O_2/P}$ were at first made at both 138 and 172, but as the result was largely insensitive to this difference and usually ended near 172, the initial guess used in later runs was 172 ± 34, again with the error expanded if the results pushed beyond one standard deviation. (The value of 34 was chosen to keep 138 at one standard deviation.) Nevertheless, both $r_{N/P}$ and $r_{-O_2/P}$ would always converge to approximately the same values, regardless of their initial guesses.

Little was known about what a realistic guess for $r_{I/P}$ at a particular depth would be, but fortunately it was fairly well-constrained by the alkalinity data in converging toward a particular answer, regardless of initial guess. Therefore a few test cases would first be run to find this value, and subsequent initial guesses for $r_{I/P}$ were taken at this value (which generally ranged from 5 ± 5 at 500 m, to 140 ± 20 at 4000 m).

While the other ratios were strongly constrained (i.e., would converge to the same value, regardless of intial guess), the $r_{C/P}$ ratio was weakly-constrained. Like the other ratios, it did show a tendency to converge to a particular value, but very weakly. For example, an initial guess of 125 might converge to a result of 118; an initial guess of 118 would then converge to a result of 114; and an initial guess of 114 would converge to 112. Similarly from the other direction, for the same data, an initial guess of 100 would converge to 107, a guess of 107 to 111, and a guess of 111 to 112. Thus a tendency toward a particular value (here 112) was still present in the carbon equation, but was very weak due to the large measurement errors of the carbon data, such that a readjustment of the initial guess was required to find this "local minimum" in the solution of the system. From the results of *Takahashi et al.* [1985] and *Peng and Broecker* [1987] we anticipated $r_{C/P}$ between 103 and 140. An initial guess was fir

therefore made at 125 ± 25, and then another run preformed using the result of the previous run (± 25) as an initial guess, and so on, until the $r_{C/P}$ ratio converged to a particular value (i.e., the result was less than 0.5 from its initial guess). In this way the results were not biased by the range of the original initial guess of 125 ± 25 but were allowed to move to that value consistent with the best fit to the data. The $r_{-O_2/P}$ results were used however in certain cases to suggest reasonable upper and lower limits on the guesses for $r_{C/P}$ based on stoichiometric grounds. Because of this sensitivity of the $r_{C/P}$ result to intial guesses however, the confidence in the $r_{C/P}$ ratio is somewhat less than suggested by the error bars on the best solutions as shown in section 4. This is another reason for which (as will be seen in section 4) the $r_{C/P}$ estimates yielded by the model are considered inconclusive, and that a more reliable estimate is deduced from the $r_{-O_2/P}$ estimate and stoichiometric limitations on the $-O_2/C_{org}$ ratio.

For the one end-member model, end-member nutrient guesses were made near those of the station in the domain exhibiting the least amount of remineralization (i.e., lowest phosphate content, highest oxygen content). In the dentrification model scenarios, ΔN^i guesses for stations 409 to 420 were chosen by observing the deviations of these stations from the straight-line trend of the other data in a NO_3 versus PO_4 scatterplot; for the other stations ΔN^i was guessed as zero. The guess for r_D was 0.0103 ± 0.0027, based on stoichiometric limitiations.

Once the observations were chosen and the parameter inital guesses established, the iterative least squares technique was applied. Several criteria were required for the results of a given run to be considered acceptable, as follows:

1. It was required that the resulting f_1^i and ΔP^i obeyed $1 \geq f_1^i \geq 0$, $\Delta P^i \geq 0$, for all stations.
2. It was required that the computed end-member properties could be verified by observed water mass properties at actual locations, as supported in the 1° × 1° atlas interpolated from the original data.
3. It was required that the final resulting value for each parameter was inside the range of the initial guess for that parameter; otherwise, the initial guesses were readjusted. (This was done to avoid any possible bias caused by making an initial guess distant from the best solution. At times, however, this criterion was not perfectly satisfiable; in such instances as close an agreement as possible was pursued.)
4. It was required that the misfits to the model equations, that is, the difference between each equation (with the computed parameters inserted) and the observed data, were within a few measurement standard deviations. After each run, such misfits were examined. Problems were often identified in this manner, as the misfits would show any systematic deviations, reveal any outliers in the data, and tell how well the model was representing the data. Most often misfits were only 2-4 times the measurement errors for the P, N, and O equations, and equal to or less than the measurement errors for the θ, C, and A equations.

If one or more of these criteria were not satisfied, the run was considered unsatisfactory. Initial guesses were revised, and/or stations added or deleted, and the run repeated.

On each surface, for a given data set, many runs were performed with various initial guesses. It was found however that the final results of the Redfield ratios (with the exception of the C_{org}/P ratio, as previously noted) were quite insensitive to initial guesses of the ratios themselves, as well as the end-member guesses. Therefore it seems unlikely that the Redfield ratio results are significantly biased by apriori expectations through the initial guesses.

The Redfield ratios were sensitive to the choice of stations used in the analysis however. Every effort was made to avoid this problem by choosing the data carefully, and performing runs with many different station combinations (particularly leaving in and out those stations that appeared as possible outliers, or that lay at the spatial edge of the domain). In this way all possible situations (within contexts supported by observations) that might give different Redfield ratio results were explored. Adjacent surfaces were also examined for consistency in the stations used, and in the Redfield ratios that resulted.

4. Results

4.1. General Remarks

Before discussing the results, some general remarks are in order. As an example, refer to the $-O_2/P$ ratio results, shown in Figure 2. The vertical axis ("depth") indicates the depth at which each neutral surface intersects a reference station near the equator (GEOSECS station 42 in the Atlantic, 251 in the Pacific, and 420 in the Indian), and is roughly the mean depth of the surface. Although on each surface several cases were run, only the high and low values are shown, to indicate the full range of resultant values. Also shown, for comparison, are the results from the studies of other authors who have also calculated the Redfield ratios from the GEOSECS data, using techniques different from ours. The legend for these symbols is shown in Table 1. As will be seen, our results are generally consistent with the other studies for all ratios, with the exception of some of the deep ocean *Minster and Boulahdid* [1987] and *Boulahdid and Minster* [1989] results.

As the equations are nonlinear, the standard deviations of the final results could not be precisely computed; the error bars shown in the following figures are estimates of one standard deviation had the system been linear. As the initial guesses were kept close to the final results, the solution of the system hopefully involved only weak nonlinearity; nevertheless, the error bars should not be interpreted too strictly.

On a particular surface, the range in results between runs is primarily due to differences in the set of stations used. The size of the error bars on the ratio estimates are primarily a function of the size of the nutrient signal relative to data measurement errors, as well as the assumed confidence in the initial guesses for the end-members and Redfield ratios. The error bars can be seen to lengthen with depth, as the remineralization signal becomes smaller.

4.2. The $-O_2/P$ Ratio

The $-O_2/P$ ratio is shown in Figure 2. In the Pacific we see that the results are approximately constant with depth at a value of 170. This is also true (within error) in the Indian Ocean, with the exception of a maximum of 200 at 1000 m. In the South Atlantic the ratios are also near 170 above 1000 m, but appear below 1000 m to be at a mean value of 120.

The anomaly at 1000 m in the Indian Ocean is odd in that it not observed in the other ocean basins. It is also peculiar because while one might expect an increase in the $-O_2/P$ ratio with depth (due to organic phosphorus being more labile than organic carbon, which is the main source of oxygen consumption), it th

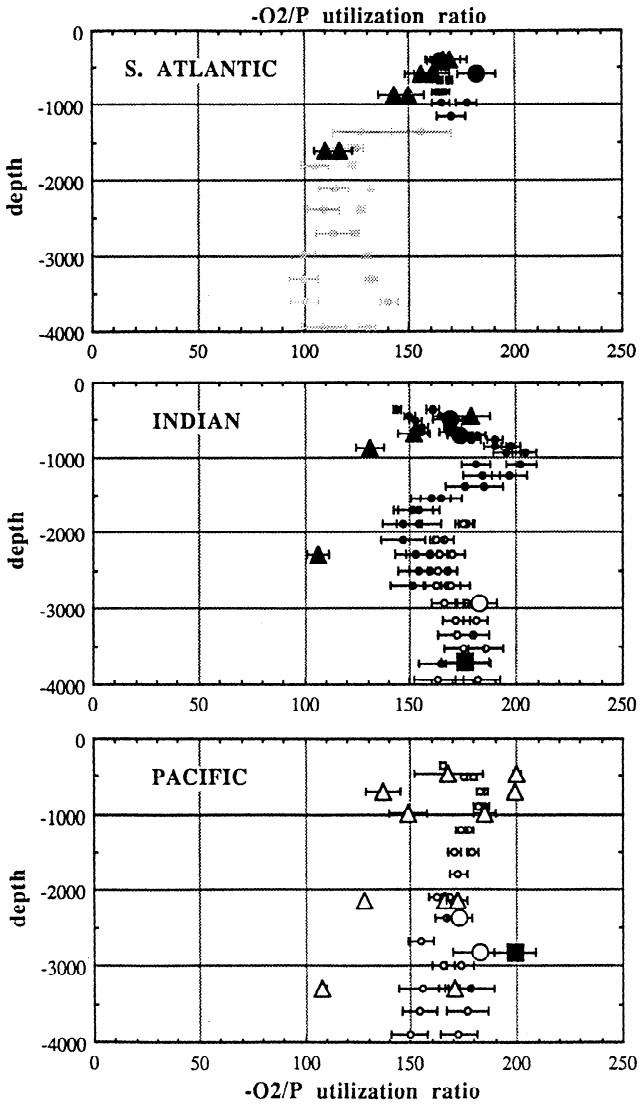

Figure 2. The $-O_2/P$ utilization ratio. Symbols are explained in Table 1, general remarks made in section 4.1, and specific remarks made in section 4.2.

rapidly decreases back to a ratio of 170. The two end-member model had been used in the analysis at these depths; looking back at the data (Figure 3), however, one realizes that the nutrient pattern might actually be due to the mixing in of a third end-member from the Indonesian Archipelago, rather than due to remineralization. Indeed, *Wyrtki* [1961] notes that, while most of the Indonesian Overflow occurs above approximately 350 m (as we had originally assumed in neglecting this end-member at depth), an inflow also occurs at 1000 m. Such inflow has also recently been supported by *Cresswell et al.* [1993]. Thus it would appear probable that the 1000 m $-O_2/P$ anomaly in the Indian Ocean, which has no good biological explanation and does not occur in the other oceans, is probably due to the fact that the Indonesian overflow was not accounted for in the analysis at these depths and has biased the results. The remaining values from the Indian Ocean then suggest an $-O_2/P$ ratio of 170 at all depths, in support of the Pacific findings.

In the South Atlantic the low values of 120 below 1000 m are also odd, as one would not expect the $-O_2/P$ ratio to decrease with depth (again, as organic phosphorus is more labile than organic carbon, one would expect the converse), and this decrease is not seen in the other basins, even though all thermocline results are identical. Looking back at the data (Figure 4), we see that in fact the remineralization signal in the deep Atlantic is practically non-existent, due to the strong mixing between the end-members at 30°N and 50°S; that is, there is a very low signal-to-noise ratio. It therefore seems most likely that the low $-O_2/P$ results in the deep Atlantic are spurious, as they make little sense in a biological context, and are based on a remineralization signal that is basically negligible.

These findings therefore support the assertion of *Broecker et al.* [1985] that the $-O_2/P$ ratio is constant with depth and basin below 400 m at a value near 175, rather than decreasing with depth as suggested by *Minster and Boulahdid* [1987]. Minster and Boulahdid were most likely led astray in the deep Atlantic, where the remineralization signal is near negligible. Furthermore, on the sigma theta surfaces 27.2 and 27.4 in Indian Ocean, Minster and Boulahdid had used a three end-member model that assumed apriori an $-O_2/N$ ratio of 9; given that the N/P correlation there is less than 16 (as will be seen), this necessitated that their $-O_2/P$ result be less than 144. It is unclear how they also obtained a low $-O_2/P$ ratio on the 27.8 surface; however this may lie in the fact that the sigma theta surface 27.8 is a poor representation of a water mass trajectory; that is, it involves a significant diapycnal flux. In the Pacific, however, *Boulahdid and Minster* [1989] do get $-O_2/P$ ratios near 170 at depth, and only obtain low values when restricting themselves to the far south Pacific. This is because the oxygen-phosphate slope appears lower south of 13°S (Figure 5). It is unclear if limiting analysis to only the South Pacific is justified, as nutrient gradients are small, and scatter is large. Indeed, fitting the remaining data in the adjacent domain north of 13°S would yield an $-O_2/P$ value of 303, and it is difficult to imagine a real biological reason why oppositely anomalous, large-scale utilization ratios would be juxtaposed, especially when above 3000 m both regions agree with a ratio near 170. (As will be shown in section 5.1, dianeutral mixing does not appear to significantly bias the lateral nutrient correlations in the deep Pacific, as it is weak and occurs in generally the same ratio as the lateral gradients.) Rather, given the scatter of the observations, and the realization that all the water in the deep Pacific between 2500 and 4000 m originates from basically the same southern end-member, it would seem more reasonable that all the Pacific data should be used in the fit. Doing so, as Boulahdid and Minster also find, yields an $-O_2/P$ ratio near 170.

In conclusion, these results suggest an $-O_2/P$ ratio of 170 ± 10 in all basins and at all depths below 400 m. An $-O_2/P$ ratio of

Table 1. Legend for Figures 2, 6, 7, and 8

Symbol	Source
Small solid circle	this study: two end-member model
Small open circle	this study: one end-member model
Small dotted circle	this study: questionable results
Large solid circle	*Takahashi et al.* [1985]
Large open circle	*Broecker et al.* [1985]
Large solid square	*Peng and Broecker* [1987]
Large solid triangle	*Minster and Boulahdid* [1987]
Large open triangle	*Boulahdid and Minster* [1989]

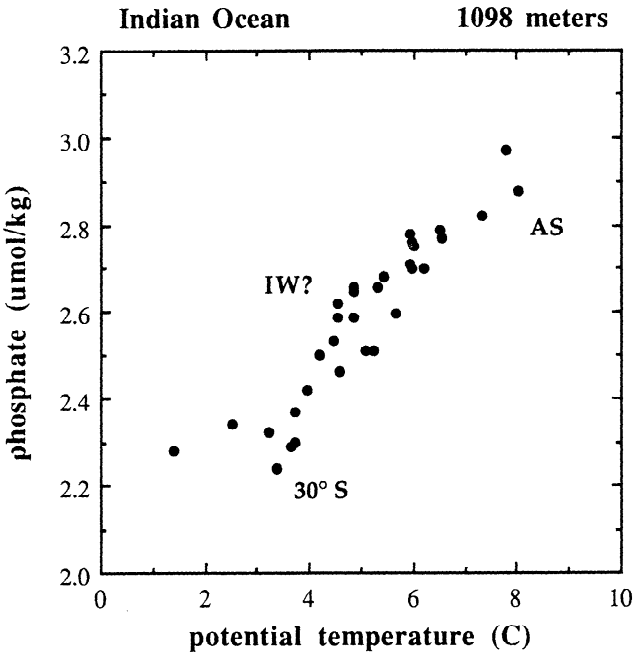

Figure 3. GEOSECS Indian Ocean data interpolated onto a neutral surface that intersects station 420 at 1098 m. Labels indicate the locations of the observations. "AS" stands for the Arabian Sea, and "IW?" for waters possibly entering from the Indonesian straits, which is in agreement with the station locations.

170 is also supported by modeling results (L. A. Anderson and J. L. Sarmiento, manuscript in preparation, 1994).

4.3. The C_{org}/P Ratio

Results for the C_{org}/P ratio are shown in Figure 6. The error bars on these estimates are rather large, particularly considering that 95% confidence is given by two error bar lengths. Where the error bars are smallest (i.e., at 500 m depth in each basin) the C_{org}/P ratio appears to center around the value of 105 ± 10. However as anthropogenic carbon was not accounted for in the model, these thermocline ratios may be underestimates (as the stronger presence of carbon near the outcrops would cause an overestimate of the "preformed" carbon concentrations, and thus an underestimate of the remineralized carbon [*Takahashi et al.*, 1985]). Because of the large error bars it is unclear if the C_{org}/P ratio varies with depth, although it appears to stay generally constant, that is, within ~ 50% of 105 at all depths. As discussed in the previous section, the values in the South Atlantic below 1000 m, which here are significantly lower than those in the deep Indian and Pacific, are most likely spurious and should be disregarded.

Although the C_{org}/P ratio is rather poorly determined, we can draw some conclusions about it based on the well-determined $-O_2/P$ ratio if we have a good estimate of the $-O_2/C_{org}$ ratio. *Martin et al.* [1987] suggest an $-O_2/C_{org}$ ratio of 1.6 for organic detritus, approximately constant with depth; however as they did not take into account the oxygen content of organic matter (i.e., the proper equation to calculate net oxygen consumption based on organic matter composition is $-O_2 = C + .25\ H + 1.25\ N - .5\ O$), and may have overestimated the organic H content (if their samples were not completely dried, thereby containing water, and as scrubbers were not used to remove any possible water from the helium carrier gas (C. Hunter, personal communication, 1993), this value of 1.6 should be thought of as an upper limit. *Laws* [1991] estimated an $-O_2/C_{org}$ utilization ratio of 1.4 ± 0.1 for phytoplankton, and a ratio of 1.5 ± 0.1 for material sinking out of the euphotic zone. However, this latter estimate is based in part on *Martin et al.*'s [1987] results, and thus might be biased high. In any case the phytoplanktonic ratio is convincing, and if we take this as the lower limit it would seem that the $-O_2/C_{org}$ ratio of water column nutrient utilization is somewhere between 1.3 and 1.6. We shall therefore assume a $-O_2/C_{org}$ ratio of 1.45 ± .15. Using our $-O_2/P$ result of 170 ± 10 then suggests an C_{org}/P ratio of 117 ± 14, i.e. a value somewhere between 103 and 131. As the $-O_2/P$ ratio was found to be approximately constant with depth, it is most probable that the C_{org}/P ratio is also constant with depth. In this way the well-constrained $-O_2/P$ ratio has proved useful in reducing the uncertainty in the otherwise poorly-determined C_{org}/P ratio. The degree of uncertainty is still significant however, a problem that can hopefully be addressed with more accurate DIC measurements in the deep Indian and Pacific (where anthropogenic carbon should not be present).

These findings disagree with those of *Martin et al.* [1987] based on sediment trap observations, which (assuming an N/P of 16) give much higher water column C_{org}/P remineralization ratios in the deep ocean. (In addition, if P is remineralized in preference to N, their C_{org}/P ratios would be even higher.) Martin et al. fit the organic flux data as a function of depth with a single power law function. As can be seen from their original data (e.g., their Figure 5), the organic fluxes change very little below 500 m, such that it is in fact the trend in the data above 500 m (and the fact that the flux has reached an approximately constant value by 500 m) that determined the best fit parameters of the fitting function. As a result, the water column remineralization ratios below 500 m, as determined by taking a quotient of the derivatives of the flux parameterizations, could

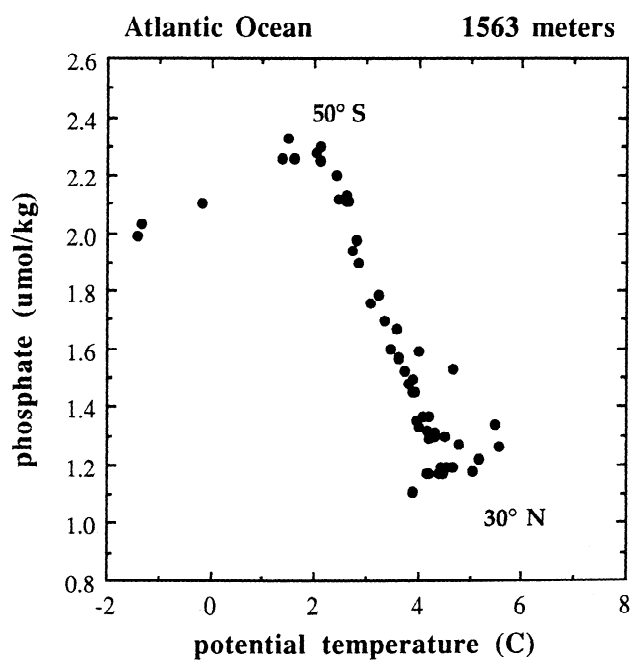

Figure 4. GEOSECS Atlantic Ocean data interpolated onto a neutral surface that intersects station 42 at 1563 m. Labels indicate the locations of the observations.

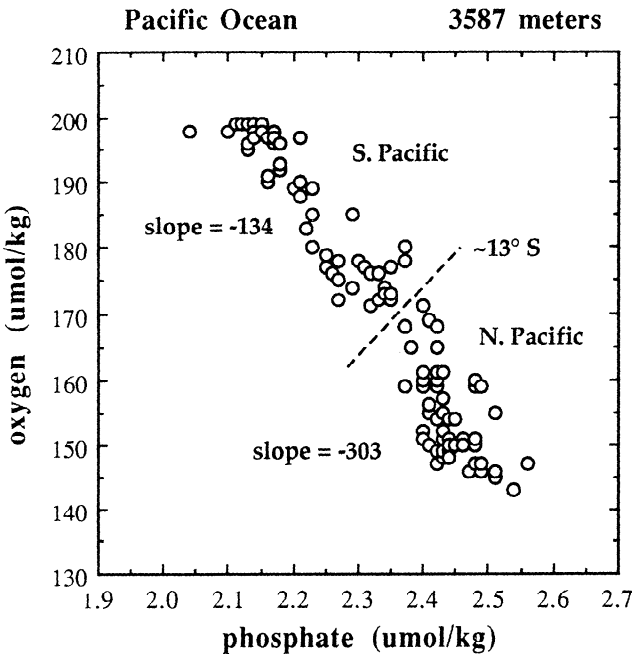

Figure 5. GEOSECS Pacific Ocean data interpolated onto a neutral surface that intersects station 251 at 3587 m. As the Pacific is basically a one end-member system at this depth, the slope of the oxygen data versus the phosphate data should indicate the $-O_2/P$ Redfield ratio. In this figure the size of the data symbols approximate the measurement error bars (one standard deviation).

easily yield spurious results not based in observation. The data show that the carbon flux below 500 m is essentially constant with depth, especially compared to the measurement variability, such that the determination of deep ocean water column remineralizaton ratios by dividing the vertical gradient of one nutrient by that of another is probably too inaccurate in the deep ocean.

Even so, the organic matter fluxing through 1000 m depth in the open ocean typically has an C_{org}/P ratio of 154 or higher [*Martin et al.*, 1987]; given that most of this material will remineralize in the ocean below, these sediment trap observations suggest that the mean remineralization ratio below 1000 m should be greater than 154, with which our conclusions disagree. This point will be taken up in section 5.2.

In summary, the C_{org}/P ratio appears approximately constant with depth and basin, at a value of 117 ± 14. As pointed out by *Takahashi et al.* [1985], such a low C_{org}/P ratio may easily be consistent with an $-O_2/P$ ratio near 172 due to the lipid content of organic matter, which is not properly accounted for in the stoichiometry of (1).

4.4. The N/P Ratio

The N/P ratio estimates are shown in Figure 7. The estimates in each basin are very similiar, with a middepth minimum. For discussion of the global N/P ratio it will be helpful to conceptually separate this profile into three distinct regimes: the 500-1000 m zone, where N/P ~ 16, the 1000-3000 m zone, where N/P ~ 12, and the 3000-4000 m zone, where N/P ~ 15.

In both the 500-1000 m and 3000-4000 m zones, the N/P ratio is approximately Redfieldian, that is, near that of the composition of planktonic biomass as determined by *Fleming* [1940]. In the 1000-3000 m zone however the N/P ratios are distinctly lower than those in the zones above and below. What is causing these low middepth ratios?

There is much evidence, from for example, sediment traps, organic decay experiments, and zooplankton excretion rates, that suggest phosphate is remineralized preferentially to nitrate [*Antia et al.*, 1963; *Menzel and Ryther*, 1964; *Corner et al.*, 1972; *Knauer et al.*, 1979], although other studies have suggested more nearly equal rates of remineralization on average [*Grill and Richards*, 1964; *Skopintsev*, 1981]. If organic phosphorus is more labile than organic nitrogen, one would expect P to be remineralized more rapidly, and therefore more shallowly, from sinking material than N. As a result the N/P remineralization ratio should increase with depth. Alternatively, if P is not remineralized preferentially to N, the remineralization ratio would be constant with depth, equal to the organic matter N/P composition (presumably ≥ 16). As such, one would expect the mean N/P ratio below 500 m to be ≥ 16. Our results, however,

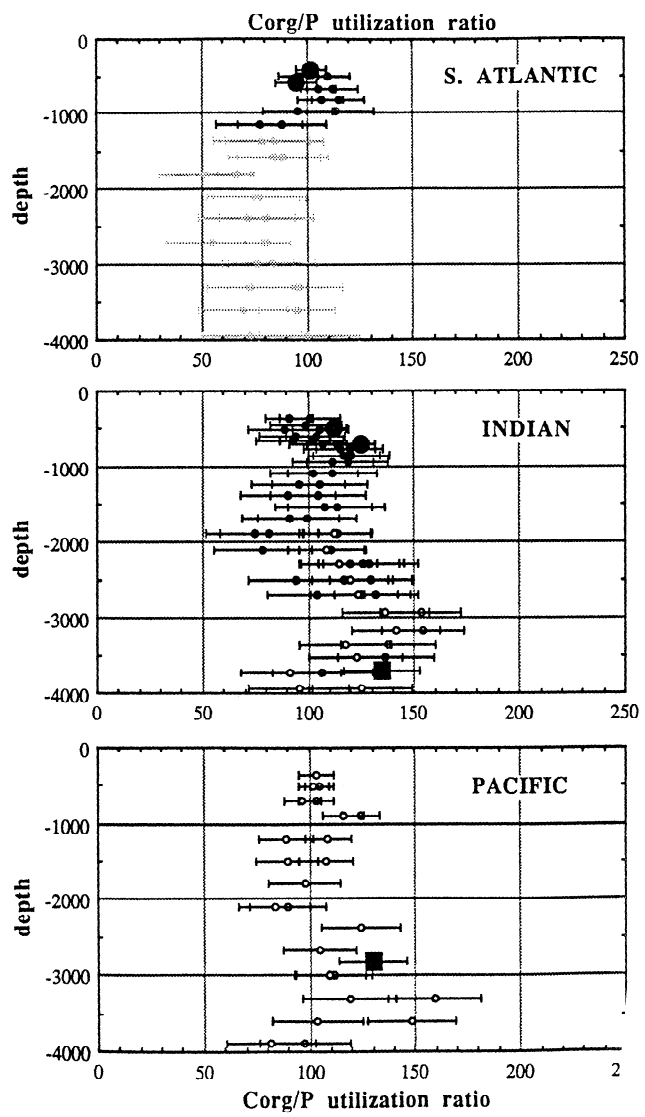

Figure 6. The C_{org}/P utilization ratio. Symbols are explained Table 1, general remarks made in section 4.1, and speci remarks made in section 4.3.

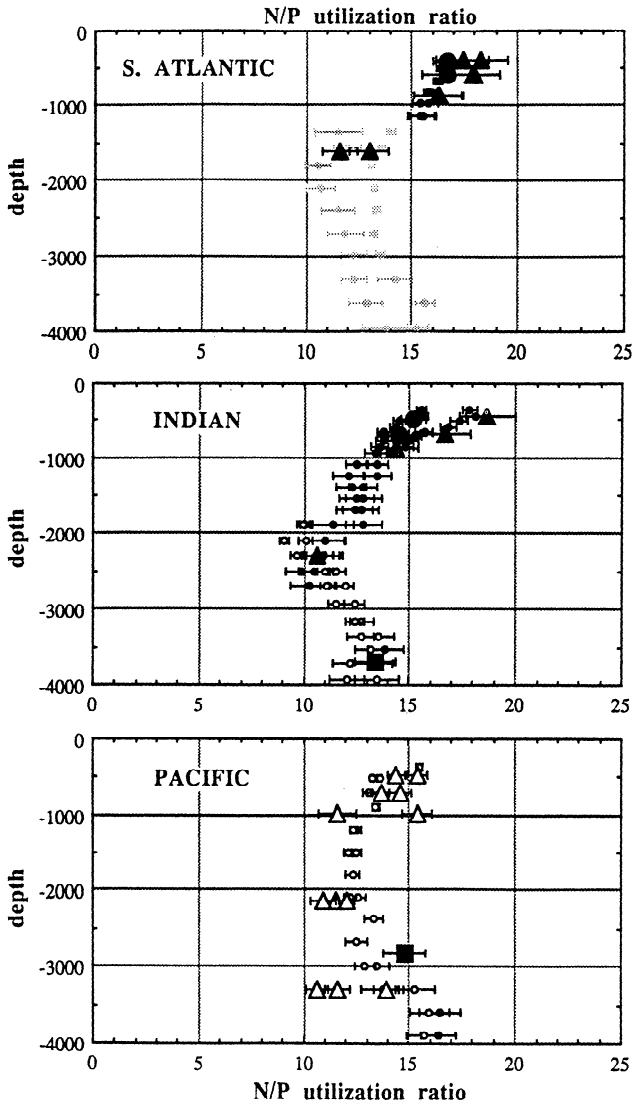

Figure 7. The N/P utilization ratio. Symbols are explained in Table 1, general remarks made in section 4.1, and specific remarks made in section 4.4.

show the N/P remineralization ratio decreasing with depth from 400 m down to 2000 m, and staying at all times ≤ 16. *Peng and Broecker* [1987], *Minster and Boulahdid* [1987] and *Boulahdid and Minster* [1989] also have observed such low deep ocean N/P values. Minster and Boulahdid have suggested that perhaps N is actually more labile than P; however, there is little other evidence in support of this possibility, and much in support of the converse. Minster and Boulahdid have alternatively suggested that this trend might be the result of all labile phosphate having been remineralized at shallower depths, such that now N is being remineralized in preference to "refractory" phosphate; yet this disagrees with our C_{org}/P ratio results which show that the amount of phosphate being remineralized relative to carbon is typical of fresh rather than refractory material.

From the organic fluxes of *Martin et al.* [1987] and the seafloor distribution, one can conclude that the nutrient increases in the 3000-4000 m zone are primarily due to the remineralization of material that has deposited on the seafloor. As nearly all such material depositing on the seafloor remineralizes, the Redfield ratios in the 3000-4000 m zone should indicate the compostion of this material. The N/P results suggest a Redfieldian composition, consistent with the $-O_2/P$ and C_{org}/P results found there. Thus it appears unlikely that the sinking matter is significantly modified (namely P preferentially removed) in its transit from the surface ocean. This is also supported by the Redfieldian N/P ratios in the 500-1000 m zone. It is therefore rather unexplainable how the N/P ratio could differ (and in particular, be lower) from 1000 to 3000 m, when it is approximately the same in the 500-1000 and 3000-4000 m zones.

The C_{org}/P and $-O_2/P$ ratios in the 1000-3000 m zone give similar evidence; they were found to be constant with depth, at approximately Redfieldian values, suggesting that the organic matter composition is not changing with depth, but staying very close to the compostion of the original ("fresh") organic material. Therefore even though P is much more labile than C_{org} it appears not to be remineralized preferentially with depth. One would then expect N, which is less labile than P, to also be remineralized in a constant ratio to C_{org} and P with depth.

Finally, 2000 m is not a depth of special biological significance in the open ocean, such that an extrema in the remineralization ratio at this depth is entirely unexpected. In summary, the observed N/P ratio middepth anomaly does not fit in well with our convential understanding of organic matter remineralization.

The possibility exists that the low N/P values obtained by the model are the result of having neglected some additional term in the model (e.g., a relative sink of nitrate or source of phosphate). In any case it would be useful to consider other factors that might be biasing these results. Therefore let us tenatively consider, should the N/P remineralization ratio actually be the classical value of 16 in this zone, what other sources or sinks of nutrients could be biasing our analysis into giving a result as low as 12.

The N/P minimum at 2000 m could be due to a relative nitrate sink or a relative phosphate source; however as the $-O_2/P$ and C_{org}/P ratios are constant with depth, and the N/P (and correspondingly the $-O_2/N$ and C_{org}/N) ratios have middepth extrema, it is most likely due to a nitrate sink. In the deep ocean the two possible sinks of nitrate are through the burial of organic matter and denitrification, both of which will be now considered.

Could the permanent burial of matter in the sediments be a preferential sink of nitrogen to phosphorus? In order that N burial decrease the N/P ratio from 16 to 12, one fourth of all the N remineralizing in the 1000-3000 m zone (both in the sediment and in the water column) would need to be permanently buried (assuming no P burial), which seems unlikely. In reality, we know that only a small fraction of the organic matter deposited on the seafloor actually becomes permanently buried. In fact, it is likely phosphorus is buried in preference to nitrogen, due to the phosphate content of skeletal hard parts and phosphorite formation [e.g., *Froelich et al.*, 1982]. Thus permanent burial of organic detritus is an unlikely explanation of the low N/P ratio.

Denitrification, which occurs under low oxygen conditions, converts nitrate to nitrogen gas, and thus is also a sink of nitrate. As denitrification in the water column below 1000 m is unlikely due to sufficiently high oxygen concentrations (except possibly in the North Pacific, which was not analyzed, and the Arabian Sea where denitrification was taken into account), this denitrificatior must be occurring in the sediments. In order to arrive at a mea N/P remineralization ratio of 12 instead of 16 in the 1000-3000 r

zone, 25% of the NO_3 remineralized in this zone must be lost to denitrification. If we assume the mean flux of organic nitrogen through 1000 m as 0.022 mol N m^{-2} yr^{-1} = 98 Tg N yr^{-1} and a 3000 m flux of 0.0075 mol N m^{-2} yr^{-1} = 28 Tg N yr^{-1} [*Martin et al.*, 1987], this explanation of the N/P anomaly requires there to be 17.5 Tg N yr^{-1} of denitrification occurring between 1000 and 3000 m. This is approximately 3 times greater than current estimates of the total deep-sea sedimentary denitrification rate, which is estimated at 4 to 7 Tg N yr^{-1}. Yet it suggests a mean sedimentary denitrification rate of .079 pmol N cm^{-2} s^{-1} in slope sediments, which is within the range of measured rates [*Christensen et al.*, 1987]; while it appears somewhat high as a mean, it is possible that denitrification rate measurements based on indirect methods are underestimates by a factor of 5 [*Devol*, 1991]. In addition, as *Christensen et al.* [1987] propose > 50 Tg N yr^{-1} denitrification in shelf sediments, this requirement may be reasonable if slope denitrification rates between 1000 and 3000 m are closer to shelf rates than previously estimated. Alternatively, it is possible that denitrification in microenvironments such as the interior of sinking particulate organic matter [*Alldredge and Cohen*, 1987] may help account for the high denitrification rate.

(One might surmise that the denitrification signal at 2000 m might actually have been advected in laterally from continental shelves upon which the neutral surfaces might impinge. However according to manganese observations [*Martin and Knauer*, 1985; *Martin et al.*, 1985], as well as oxygen distributions [*Levitus*, 1982], the influence of continental shelves reach at most 1000 m depth in the ocean interior, and thus cannot explain the 2000 m anomaly.)

Why would the denitrification signal have a maximum at 2000 m, and not significantly appear in the 500-1000 m and 3000-4000 m zones? Perhaps the denitrification rate (per unit area), which should decrease with depth (on account of organic and total deposition rates decreasing with depth and distance from shore), is counteracted by the decrease in remineralization rates and the increase of seafloor surface area with depth to create a relative maximum in the denitrification-to-remineralization signal. That is, the denitrification signal might not appear above 1000 m nor below 3000 m due to high remineralization rates in the former and low denitrification rates in the latter. Assuming the Redfield ratio estimate between 500 and 1000 m is not biased by denitrification by more than 0.5, the mean sedimentary denitrificaton rate there cannot be greater than 0.078 pmol N cm^{-2} s^{-1} (calculated from remineralization rates based on the *Martin et al.* [1987] fluxes and *Levitus* [1982] bathymetry). This is in close agreement with the 1000-3000 m requirement, such that the N/P values between 500 and 3000 m are explainable if the denitrification rate in both the 500-1000 and 1000-3000 m zones is approximately .078 pmol N cm^{-2} s^{-1}. Below 3000 m, as the "apparent" Redfield ratio is approximately 15, the mean sedimentary denitrification rate should be near 0.0015 pmol N cm^{-2} s^{-1}, which is 53 times less than the required 1000-3000 m rate. The primary problem with this explanation is that there are no clear observations that support such a sharp distinction between slope and deep-sea denitrification rates. However, high slope denitrification rates would be consistent with the view of high margin productivity causing organic deposition rates to margin sediments that are much higher than deposition rates in the ocean interior [*Jahnke and Jackson*, 1987; *Jahnke et al.*, 1990]. Organic material carried from shelves and deposited onto slopes would also be conducive to higher slope denitrification rates. (The denitrification estimates are also dependent on possible errors in the *Martin et al.* [1987] fluxes, and their application in these calculations.)

A second problem with this theory is that the required high slope denitrification rates puts our understanding of the N cycle further out of balance, with nitrate sinks exceeding sources by an even larger amount (i.e., another 12 Tg N yr^{-1}) than previously estimated. Despite these problems, however, denitrification seems the most likely explanation for the N/P anomaly.

In summary, our estimates confirm the results of *Takahashi et al.* [1985] of a Redfieldian N/P ratio of 16 in the thermocline, but also those of *Peng and Broecker* [1987], *Minster and Boulahdid* [1987], *Boulahdid and Minster* [1989] which show the N/P ratio to be noticeably lower in the deep ocean. We believe it is likely that sedimentary denitrification is responsible for this deep ocean minimum in the N/P utilization ratio estimates, and that the actual N/P remineralization ratio of organic tissue is approximately constant with depth, as this would be most consistent with conventional thinking on the lability of organic phosphorus, and with our other utilization ratio results.

4.5. The C_{org}/C_{inorg} Ratio

As it is more common in the literature to examine the C_{org}/C_{inorg} ratio than the C_{inorg}/P ratio as calculated here, we divide the C_{org}/P ratio results by the C_{inorg}/P results, propagating the errors, to present C_{org}/C_{inorg} ratio estimates, shown in Figure 8. In the thermocline the C_{inorg}/P ratio is very small, such that the C_{org}/C_{inorg} estimate is very large, with very large associated errors. In the deep ocean, however, the estimates are more robust.

At 400 m there may be significant interbasin differences. In the South Atlantic the mean C_{inorg}/P ratio is very small (2.5 ± 2.5), such that assuming an C_{org}/P of 117, the C_{org}/C_{inorg} ratio is approximately 47, much higher than the estimate of *Takahashi et al.* [1985] of roughly 12. However, as the error bars of our estimate are extremely large, and indeed encompass the *Takahashi et al.* [1985] estimate, it is difficult to draw a firm conclusion. In the Indian Ocean at 400 m the C_{org}/C_{inorg} ratio is approximately 8 ± 4, and in the Pacific, 6 ± 1. Therefore at 400 m, it appears that there may be very little calcium carbonate dissolution in the Atlantic, but significant amounts in the Indian and Pacific.

Below 500 m the basins come into closer agreement, with the C_{org}/C_{inorg} ratio decreasing to about 3 by 1000 m and to 1 by 4000 m (again with the deep South Atlantic being considered unreliable). These ratios suggest that 25% of the carbon regenerated at 1000 m and 50% of the carbon regenerated at 4000 m is from $CaCO_3$ dissolution. Note that the C_{org}/C_{inorg} ratio of 1 is consistent with the composition of material caught in sediment traps at these depths [*Honjo et al.*, 1982; *Wefer and Fischer*, 1993]; assuming remineralization of most of the organic carbon reaching these depths, this suggests dissolution of most of the calcium carbonate.

These results therefore suggest significant dissolution of calcium carbonate above the calcite lysocline, which is roughly a 3000 m depth in each of the regions analyzed. One possibility i that this calcium carbonate is in the form of aragonite, whic reaches undersaturation at approximately 1500 m in the south t 400 m in the north in both the Indian and Pacific over the areas (analysis, yet is below 1500 m in the South Atlantic, consiste

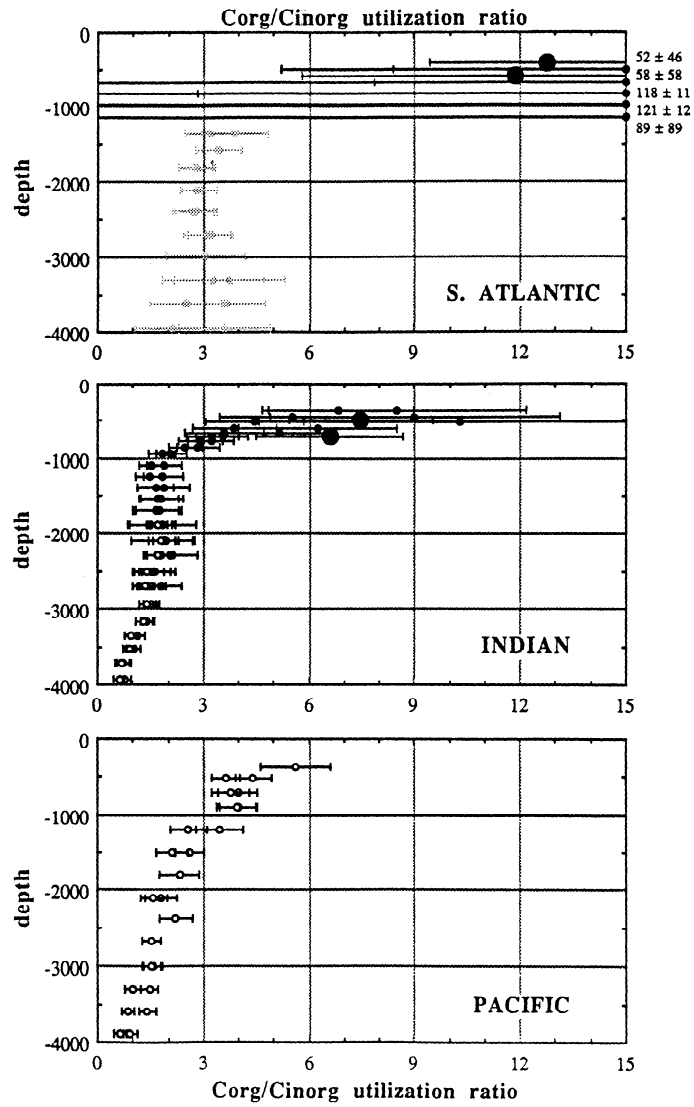

Figure 8. The C_{org}/C_{inorg} utilization ratio. Symbols are explained in Table 1, general remarks made in section 4.1, and specific remarks made in section 4.5. The South Atlantic estimates depicted at the value "15" are actually much higher, at the values indicated.

with the lack of dissolution found there. However, observed aragonite fluxes are generally small; for example in the North Pacific aragonite fluxes can account for only 7-13% of the inorganic carbon dissolution evidenced by alkalinity changes there [*Fabry*, 1989, 1990]. There is also evidence of calcite dissolution above its lysocline; for example, *Bishop et al.* [1986] found that the flux of coccoliths in the Panama Basin to decrease with depth above the calcite lysocline. A possible mechanism is that calcite dissolves in microenvironments, for example, calcite-undersaturated regions within marine snow aggregates and fecal pellets, or in the guts of animals [*Fabry*, 1990]. Calcite may also dissolve in the upper ocean in undersaturated sediment porewaters [*Emerson and Bender*, 1981].

Because of their apparent interbasin variability, and the fact that high-latitude regions were not analyzed, the C_{org}/C_{inorg} ratio results presented here should not be taken as necessarily representative of global mean values. Furthermore, one would expect these ratios to be functions of latitude on sub-basin length-scales. Further investigation is needed.

5. Discussion

5.1. Dianeutral Mixing

The possible change in nutrients on a given neutral surface due to dianeutral advection and diffusion was assumed to be negligible in this study. Neutral surfaces (which have cross-surface fluxes smaller than isopycnal surfaces by about an order of magnitude [*McDougall*, 1987b]) were chosen in the first place so that cross-surface mixing would be negligible. It is, nevertheless, important to evaluate the effect dianeutral mixing might have had on these estimates, as a potential source of error.

According to *McDougall and You* [1990, p. 13,272], dianeutral diffusion is generally negligible, although dianeutral advection due to cabbeling and thermobaricity can be significant. The change in nutrients in a water parcel due to dianeutral advection would be

$$\delta N/\delta t = -\omega\, dN/dz \quad \rightarrow \quad \delta N = -\delta t\, \omega\, dN/dz \qquad (3)$$

where N stands for an arbitrary nutrient, ω is the dianeutra

velocity, z the dianeutral coordinate, and δt is the time the water parcel is subject to dianeutral advection. As ω is generally negative (i.e., downward) [*McDougall and You*, 1990], we see that dianeutral advection will cause, for example, a decrease in phosphate concentrations above the phosphate maximum, and generally an increase in phosphate below the phosphate maximum.

McDougall and You [1990] show there to be a fair amount of spatial variability in dianeutral velocities on a given neutral surface; however, in order to make a simple estimate, based on their maps we assume the mean dianeutral velocity ω over the regions analyzed is -0.02×10^{-7} m s^{-1} = -0.06 m yr^{-1} at all depths below 500 m, and that δt is 500 years. The total amount of dianeutrally advected nutrient on a given neutral surface δN is thus (0.3 m) × dN/dz, which is shown in Table 2 for the regions analyzed. Given these estimates, we can recalculate the "true" Redfield ratios by accounting for these biases due to dianeutral mixing, that is,

$$r_{N/P}^{true} = \Delta N^{true}/\Delta P^{true} = (\Delta N - \delta N)/(\Delta P - \delta P) \quad (4)$$

such that the bias due to dianeutral mixing δr is

$$\delta r = r_{N/P}^{estimated} - r_{N/P}^{true} = \Delta N/\Delta P - (\Delta N - \delta N)/(\Delta P - \delta P) \quad (5)$$

The results of these calculations are shown in Table 3.

As can be seen in Table 3, accounting for dianeutral mixing has caused little difference in the N/P estimates, and the C_{org}/P estimates are very insignificantly biased relative to their error bars. The systematic error from neglecting dianeutral mixing on the $-O_2/P$ ratio estimates are also generally negligible below 1000 m; however, above 1000 m the $-O_2/P$ ratio appears to have been overestimated by 5, that is, that the true ratio may be closer to 165. (The same holds for the Indian Ocean between 1000 and 2000 m, and thus dianeutral mixing may be the cause for part, namely 5, of the high $-O_2/P$ anomaly centered at 1000 m depth there.) Again, these calculations assume $\omega\delta t$ = -0.3 m, and if this quotient is higher than this, these errors will be higher, in direct proportion. However, based on the maps of *McDougall and You* [1990] $\omega = -0.02 \times 10^{-7}$ m s^{-1} seems to be a reasonable upper limit for the regions analyzed, as does δt = 500 years. Thus the conclusions from section 4 concerning the N/P and C_{org}/P results, as well as the statement that the $-O_2/P$ ratio is approximately constant with depth below 500 m at 170 ± 10, still seem to be true.

Of course these calculations of the effect of dianeutral mixing are very simplistic. In view of the importance of cross-surface mixing on nutrient gradients in the upper ocean as suggested here, a method that properly accounts for dianeutral mixing appears necessary to determine Redfield ratios from nutrient gradients in the upper several hundred meters.

Table 2. Increase in Nutrients on Neutral Surfaces due to Dianeutral Advection

Depth	δP	δN	δO_2	δC
	South Atlantic			
500-1000 m	-.021	-.30	-0.5	-2.3
1000-2000 m	.015	.21	-1.3	0.5
2000-3000 m	.001	.02	-0.3	-0.1
3000-4000 m	-.007	-.09	0.2	-0.8
	Indian			
500-1000 m	-.039	-.53	1.7	-5.1
1000-2000 m	.003	.02	-1.6	-0.7
2000-3000 m	.003	.03	-0.8	0.0
3000-4000 m	.002	.02	-0.6	0.4
	Pacific			
500-1000 m	-.043	-.70	0.8	-5.9
1000-2000 m	.002	.03	-0.3	-1.6
2000-3000 m	.003	.03	-0.5	0.1
3000-4000 m	.005	.07	-1.0	0.9

Estimated from (3), using $\omega\delta t$ = -0.3 m, and with z approximated as the vertical coordinate. The values of δP, δN, δO_2, and δC are in μmol/kg.

Table 3. Biases in Redfield Ratio Estimates Presented in Section Four Due to the Neglection of Dianeutral Mixing

Depth	ΔP, μmol/kg	$\delta r_{N/P}$	$\delta r_{-O_2/P}$	$\delta r_{C/P}$
	South Atlantic			
500-1000 m	0.80	0.0	+5	0
1000-2000 m	(0.70)	0.0	-2	-2
2000-3000 m	(0.60)	0.0	0	0
3000-4000 m	(0.60)	0.0	+2	0
	Indian			
500-1000 m	1.00	+0.1	+5	-1
1000-2000 m	0.20	-0.1	+6	-5
2000-3000 m	0.50	0.0	+1	-1
3000-4000 m	0.40	0.0	+1	0
	Pacific			
500-1000 m	1.00	0.0	+6	-1
1000-2000 m	0.60	0.0	0	-3
2000-3000 m	0.35	0.0	0	-1
3000-4000 m	0.25	0.0	+1	+1

These estimates are based on (5), using δP, δN, δO_2, and δC from Table 2. ΔP was assumed as shown, based on the maximum size of the remineralization signal, averaged over the neutral surfaces in each zone. (The value for ΔP in the South Atlantic below 1000 m is as was assumed in the model, used here to see how dianeutral mixing might have biased the calculations; however, in reality ΔP in the South Atlantic below 1000 m is near zero, and the Redfield ratio estimates based on the nutrient trends are spurious.) ΔO_2 was taken as $-170 \times \Delta P$, ΔC_{org} as $117 \times \Delta P$, and ΔN as $16 \times \Delta P$ above 1000 m, $12 \times \Delta P$ between 1000 and 3000 m, and $15 \times \Delta P$ below 3000 m, consistent with the section 4 results.

5.2. Fresh Organic Matter Delivery to the Deep Ocean

These Redfieldian utilization ratio estimates, based on the observed correlated changes in nutrients in the global ocean suggest that the primary substrate of remineralization in th ocean between 400 and 4000 m has a composition close to that c fresh, undecomposed planktonic biomass. This suggests rapi transit of material from the surface ocean. It is therefore unlike that matter exported as DOM from the euphotic zone could be t primary substrate of remineralization below 400 m, as it

difficult to see how DOM would be able to maintain a fresh composition (i.e., not become P depleted) in the time it would take to reach the deep ocean. In fact, these Redfieldian ratios provide the constraint that if DOM remineralization is important in the deep ocean DOM must have a Redfieldian composition, and given that DOP values below 500 m are typically 0.01 μmol/L [*Ridal and Moore*, 1990], this means that only 1 μmol/L of DOC in the deep ocean can be labile (although more DOC could be labile if DOM remineralization is effectively unimportant in comparison with POM remineralization). Particulate organic matter (POM), on the other hand, could easily explain the quick transport of "fresh" material to the deep ocean, and therefore seems the likely source of most organic material remineralizing in the deep ocean.

While POM is often observed to be produced in a Redfieldian composition [e.g., *Small et al.*, 1983] and to have a Redfieldian composition near the sea surface [*Copin-Montegut and Copin-Montegut*, 1983; *Karl et al.*, 1984, 1988; *Knauer and Martin*, 1981a; *Martin et al.*, 1987; *Pace et al.*, 1987; *Treguer et al.*, 1990], observations from sediment traps, bottles and insitu pumping have generally shown P and N to be preferentially and rapidly removed from sinking organic material, such that by 400 m it commonly has compositional ratios of N/P ~ 20-35, C_{org}/P ~ 180-300, and C_{org}/N ~ 8-10 [*Bishop et al.*, 1977, 1986; *Copin-Montegut and Copin-Montegut*, 1983; *De Baar et al.*, 1983; *Dymond and Lyle*, 1985; *Honjo*, 1980; *Honjo et al.*, 1982; *Karl et al.*, 1984, 1988; *Knauer and Martin*, 1981a, b; *Knauer et al.*, 1979; ~~*Martin et al.*~~, 1987; *Nair et al.*, 1989; *Pace et al.*, 1987; *Treguer et al.*, 1990; *Wefer et al.*, 1982]. As this matter fluxing through 400 m almost completely remineralizes in the ocean below, its composition should equal the mean remineralization ratio below 400 m; yet these ratios are much larger than those shown in section 4. Why do these observations disagree with ratios based on nutrient gradients?

One difficulty with obtaining samples involves the loss of material due to cell lysing, elemental desorbtion and mechanical breakdown [*Knauer and Martin*, 1981b; *Gardner et al.*, 1983; *Knauer et al.*, 1984; *Dymond and Lyle*, 1985]. As one would expect the material that does degrade to be of more labile composition than the material that does not, the elemental composition of sampled material may be biased toward higher-than-Redfieldian values. For example, high dissolved PO_4 concentrations have been found in sediment trap preservative solutions [*Knauer and Martin*, 1981b] and in water that had been used to wash samples [*Wefer et al.*, 1982]. *Dymond and Lyle* [1985] note a preserved trap experiment at 700 m depth in which 60-90% of the particulate P was released into solution. Apparently, this P had been released from the sinking matter. It is unclear whether this P originated from a biogenic constituent of the organic particle, or simply had been weakly adsorbed onto the particle surface from the ambient seawater. However, even if the PO_4 had simply been adsorbed onto the particle surface, it would still contribute to the vertical flux of P as the particle sank, and thus should in any case be included as part of the elemental flux. When this soluble P is included in ratio calculations of *Knauer and Martin* [1981b] and *Wefer et al.* [1982], which otherwise exhibit typically high C_{org}/P and N/P ratios, the C_{org}/P and N/P ratios become Redfieldian and even less, suggesting that the vertical transport of nutrients by particulate matter may indeed be Redfieldian.

If P is lost from particulate organic matter samples, it seems possible that N and C_{org} also are. N is certainly known to be lost from unpreserved traps [e.g., *Karl et al.*, 1984]; while these observations show a POM C_{org}/N ratio that is typically high, if the NH_4 in the trap solutions are included, the C_{org}/N_{total} ratios turn out to be Redfieldian or less, even down to 750 m (their deepest trap). POC has been observed to convert to DOC in preserved sediment trap collection cups by *Smith et al.* [1992] and by *Lee and Fisher* [1992]. Thus it seems possible that sinking particulate material actually may be close to Redfieldian but that significant amounts of labile and/or soluble nutrient components are lost from the material.

Another possibility is that the composition of the POM flux as most often observed is not representative of the long-term mean contribution. While, as mentioned above, POM flux ratios are most typically observed to be higher than Redfieldian, at times Redfieldian POM fluxes have been measured, even at great depths [*Copin-Montegut and Copin-Montegut*, 1983; *Honjo*, 1978; *Honjo et al.*, 1982; *Lochte and Turley*, 1988; C_{org}/N ratio: *Dymond and Lyle*, 1985; *Wefer et al.*, 1982]. In particular, it has been demonstrated that POM fluxes appear to be more Redfieldian beneath regions of high productivity [*Knauer et al.*, 1979; *Pace et al.*, 1987] and it is possible that the majority of the organic flux to the deep ocean occurs under such high productivity regions rather than the larger, oligotrophic regions. *Jahnke and Jackson* [1987] contend that half of the input of organic matter to seafloor may occur near the highly productive ocean margins. Transport of material from high-productivity shelf regions may also be important in the deep-ocean interior [*Walsh*, 1991].

High productivity events (e.g., blooms, of various sizes) are similarly likely to deliver Redfieldian fluxes to the deep ocean. This is particularly true if the vertical delivery events are sporadic (i.e., highly concentrated) in space and time, thereby avoiding predation and degradation, qualities which would also make them difficult to sample. *Michaels and Silver* [1988] say that large algal cells, which are the dominant source of sinking organic matter, exist in sporadic patches even in oligotrophic regions, and are likely to be undersampled; furthermore, episodic grazer events that may control the average, long-term export of matter from the surface ocean are similarly patchy and likely to be undersampled. *Wakeham and Canuel*'s [1988] study of lipids in suspended and sinking matter support the idea of a downward flux of "fresh" algal cells that is apparently not sampled by sediment traps. *Jahnke et al.* [1990] also suggest that short times series trap measurements undersample important episodic events, as the VERTEX sediment trap fluxes were three times too low to explain benthic oxidation rates, a point later confirmed by *Smith et al.* [1992].

A final possibility is that living organisms may transport elements in ways that cannot be easily sampled. Vertically migrating organisms can ingest organic material at one depth, and respire or excrete it at another (perhaps even as nutrients or DOM), thus vertically transporting organic matter in their guts [*Parsons et al.*, 1984; *Angel*, 1989]. Such organism migrations could transport labile organic material vertically quite quickly and extensively. Organic matter may also be significantly transported by the living biomass of vertically migrating organisms themselves [*Silver and Gowing*, 1991], for example, if organic matter is grazed (going into permanent animal biomass at one depth, and the grazer ends its life cycle (e.g., is eaten) at different depth. Given that organisms have near Redfieldian

compositions, this would contribute to a Redfieldian vertical flux.

Thus there are several problems that sampling methods may encounter in determining the elemental composition of the vertical organic flux. The correlated nutrient gradients in the ocean, once the "preformed" nutrient concentrations of mixing water masses have been taken into account, clearly indicate that the mean composition of material degrading in the deep ocean (i.e. below 400 m) is Redfieldian. Further support for Redfieldian ratios in the deep ocean are given by numerical models, which, as will be discussed in L. A. Anderson and J. L. Sarmiento (manuscript in preparation, 1994), require an $-O_2/P$ utilization ratio of 172 or less in the deep ocean; given the probable hydrogen content of organic matter, this means the C_{org}/P ratio in the deep ocean must be near Redfieldian.

These Redfieldian utilization ratio estimates therefore support the idea that high-productivity regions and/or sporadic events are responsible for the dominant flux of organic matter to the deep ocean. While it is therefore possible that the remineralization ratios are different (namely higher) in low-productivity regions (and periods), high-ratio organic matter fluxes appear to contribute very little nutrients to water masses below 400 m. Therefore on a basin-wide and time-mean scale we can effectively treat the nutrient utilization ratios as constant at Redfieldian values.

These Redfieldian ratios suggest that the material remineralizing in the deep ocean is primarily not high C_{org}/N and C_{org}/P "leftovers" from the upper ocean, but rather fresh material that has apparently escaped degradation in the upper ocean. On a theoretical basis, only fluxes that are sporadic in time and space, of large magnitude, and/or are fast-sinking, and thus escape predation in the upper water column, are likely reach the deep ocean (A. Michaels, personal communication, 1991). As previously discussed, fluxes from such sporadic, high-productivity events typically have Redfieldian composition. Therefore it is not unreasonable that the delivery of organic matter to the deep ocean (i.e., below 500 m) be Redfieldian in the mean.

5.3. High-Latitude Regions and the Upper Ocean

The North Atlantic and the North Pacific thermocline were not analyzed due to the existence of three or more end-members, while the southern ocean was not analyzed due to weak lateral nutrient gradients. It is possible that the utilization ratios in these areas are different from those in the regions we did analyze. Of special importance are the high latitudes, as they are regions of high productivity, and as the nutrient utilization in these regions help determine preformed deep ocean nutrient concentrations. Since the biota in high latitude waters are not PO_4 or NO_3 limited, and are a different assemblage of organisms than in lower latitudes, with possibly different ecosystem structure and behavior (and therefore possibly different nutrient remineralization pathways), these regions may or may not have different water column nutrient utilization ratios.

Perhaps more importantly, another region that was not analyzed by this or similar studies [e.g., *Takahashi et al.*, 1985] is the ocean above 400 m, due to inapplicability of the technique (see section 2). *Sambrotto et al.* [1993] have suggested that the C_{org}/N nutrient utilization ratio in the surface ocean is higher-than-Redfieldian, as one might expect if nitrogen is preferentially remineralized to carbon there. Other studies however suggest lower-than-Redfieldian ratios [*You and Tomczak*, 1993; *Reverdin et al.*, 1993, p. 16,292]. If any of these findings are true, it would suggest a possible dichotomy in the water column nutrient utilization ratios, between the upper ocean, where slowly sinking, suspended and dissolved organic matter may play significant roles in the preferential recycling of certain elements with depth, and therefore non-Redfieldian ratios, and the deep ocean (below 400 m), which is apparently only visited occasionally by inputs of fresh matter that somehow escape the upper ocean undegraded, and is characterized by Redfieldian ratios.

6. Summary

The net-ecosystem nutrient utilization ratios between 400 and 4000 m, as determined by the observed nutrient distribution gradients in the global ocean, can be summarized as follows:

The $-O_2/P$ ratio is 170 ± 10, constant with depth and basin.

The C_{org}/P ratio, as suggested by the data analysis and stoichiometric grounds, is 117 ± 14. The C_{org}/P ratio appears constant with depth and basin.

The N/P utilization ratio appears to decrease with depth from a value of 16 at 400 m to a value of 12 at approximately 2000 m depth, and then increases back to ~15 by 4000 m depth. (Correspondingly, the C_{org}/N ratio increases from approximately 7 at 400 m to 9 or 10 at 2000 m, decreasing somewhat with further depth.) It is speculated that this trend is due to sedimentary denitrification, the signal enhanced at middepths due to the small amount of remineralization relative to denitrification there, and that the actual organic material reaching depths below 400 m has a Redfieldian nitrogen composition. This would suggest that the N/P remineralization ratio (without denitrification) is 16 ± 1, constant with depth and basin.

In the Indian and Pacific the C_{org}/C_{inorg} ratio decreases from approximately 7 ± 3 at 400 m to 3 at 1000 m to 1 at 4000 m. In the Atlantic between 400 and 1000 m the ratio may be near 50, but because of large error bars this is difficult to say. In any case the C_{org}/C_{inorg} ratio appears to vary with basin in the upper water column, and one would expect it to vary with latitude on the sub-basin scale. It should also be remembered that the high latitudes, which tend to have low $CaCO_3$ production relative to organic matter production and therefore may have higher C_{org}/C_{inorg} utilization ratios, were not included in the analysis. As such a mean based on these profiles may underestimate the global-mean C_{org}/C_{inorg} ratio. For these reasons these C_{org}/C_{inorg} results should be considered as preliminary, and further investigation, particularly accounting for meridional variation, is needed.

Thus the $P/N/-O_2/C_{org}$ ratios of remineralization below 400 m appear to be constant with depth and basin at $1/16 \pm 1/170 \pm 10/117 \pm 14$. Including denitrification, the nutrient utilization ratios decrease to approximately $1/12 \pm 2/170 \pm 10/117 \pm 14$ in the 1000-3000 m zone. These findings generally confirm the studies of *Takahashi et al.* [1985] and *Broecker et al.* [1985].

These Redfieldian remineralization ratios suggest that the flux of organic matter to the deep ocean is dominated by fast-sinking matter produced by sporadic, high-productivity events. In addition, the C_{org}/C_{inorg} ratio suggests that a significant amount of calcium carbonate dissolution occurs above the calcite lysocline, at least in the Indian and Pacific.

As these are long-term, basin-wide, net-ecosystem utilization ratios, they may not be applicable on short timescales or length

scales, or to separate ecosystem components. Also, these ratios may not be applicable to high-latitude regions or the ocean above 400 m.

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