The effect of the water column oxygen minimum zone on sedimentary organic matter diagenesis

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Early organic matter diagenesis in continental margin sediments is fueled by the rain of carbon from the surface layer. Previous workers have found that sediment trap carbon fluxes are proportional to primary productivity and decrease as a power function of water column depth, e.g. Flux = $Flux_0 \times depth^{-\alpha}$ Martin, *et al.*, 1987). The water column decrease results from progressively more organic matter oxidation with time as particles settle. As sediment trap flux is a measure of the carbon rain rate at that depth, a similar depth relationship would be expected for sedimentary rate processes. To test this hypothesis, we have occupied two transects: one off the coast of northwest Mexico (~20° N) and a second off the northwest coast of Washington State, U.S.A. (~47° N: Devol and Christensen, 1994). Off Mexico, the sediments in the 150–600 m depth interval are in contact with the oxygen deficient waters of the eastern tropical North Pacific, while off Washington State oxygen is present in the water column at all depths.

Methods and results

On both transects sedimentary carbon oxidation rates were determined by a combination of methods. *In situ* benthic flux measurements were measured for dissolved oxygen, nitrate and phosphate. Sulphate reduction rates were determined by the $^{35}SO_4$-sulphate reduction technique, and pore water profiles of oxygen, nitrate phosphate, manganese and iron were measured. Sedimentary carbon oxidation rates were estimated assuming that all reduced species produced, e.g. S^{2-}, Mn^{2+}, were reoxidized by oxygen.

Off Mexico, carbon oxidation rates were about 5 mmoles m^{-2} d^{-1} on the shelf and decreased only by about a factor of 2.5 between 100 m and 1000 m (Fig. 1). From 1000 m to 2000 m carbon oxidation rates actually increased again. Conversely, off Washington state, carbon oxidation rates on the shelf were faster, about 15 mmoles m^{-2} d^{-1}, and attenuated more rapidly such that they reached the same values as off Mexico by 1000 m. When the Mexican margin data was fit as a power function of depth the attenuation exponent, α, was -0.38, and the significance of the relationship was weak, r^2 = .043. Conversely, the fit to the Washington margin data gave an attenuation exponent, of -0.87, and the r^2 was a more robust 0.86.

At all shallow stations (100 m to 1000 m) on both transects, pore-water nitrate was exhausted in the upper 1 cm. Sediments from the shallow Washington State cores had low levels of dissolved manganese but distinct subsurface peaks in dissolved iron. As water column depth increased below 1000 m, subsurface peaks in dissolved manganese became

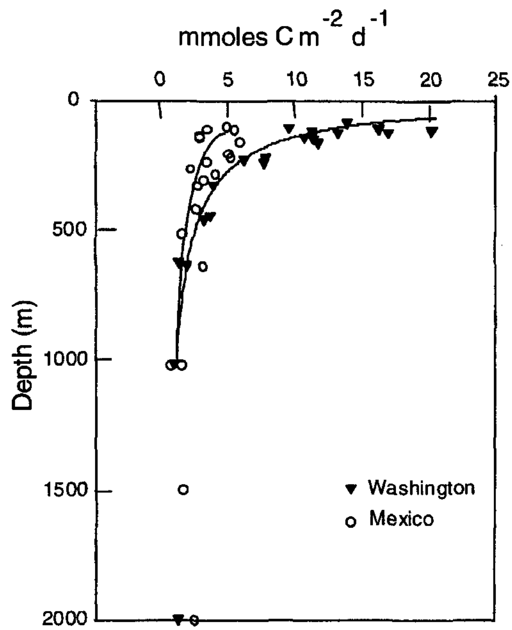

FIG. 1. Sedimentary carbon oxidation rate versus depth for the Washington state transect (solid symbols) and Mexican transect (open symbols). Curve fits are to the power function as described in the text.

more prominent while the iron peak decreased in magnitude and shifted deeper. Off Mexico, all stations within the oxygen deficient zone had nearly undetectable levels of both dissolved metals. On both transects downcore increases in both metals were associated with the depletion of nitrate and the appearance of measurable NH_4. Overall, dissolved metal concentrations reached much higher levels in the Washington State transect than in the Mexican transect.

Comparison of C:N:P flux ratios from the two transects revealed significant differences between the two continental margins. C:N:P flux ratios were calculated as the ratio of the carbon oxidation rate to the flux of combined nitrogen out of the sediments to the phosphate flux out of the sediments. C:N:P flux ratios for the Mexican margin averaged 17.2:2.0:1. This is a C:N ratio of 7.4 and an N:P ratio of 2.3. Off Washington State the flux ratio was 228:11.5:1, yielding a C:N of 19.8 and and N:P of 11.5.

Discussion

On the Washington State transect sedimentary carbon oxidation rates decreased as a power function of depth as would be predicted from sediment trap studies. Furthermore, the attenuation coefficient, $\alpha = -0.85$, was in excellent agreement with values determined from traps studies (Martin *et al.*, 1987; Bender *et al*, 1992). In contrast, rates of Mexico decrease much less, $\alpha = -0.38$, and the relationship was much weaker. We interpret these differences between the attenuation coefficients as a change in the relationship between rain rate and depth brought about by the oxygen deficient zone off Mexico. We hypothesize that the lack of oxygen in the water-column greatly reduces oxidation of sinking organic detritus, which results in a much larger portion of the carbon flux surviving to depth. The decrease in oxidation might be due to severely reduced zooplankton populations in the oxygen deficient zone (King *et al.*, 1978) or it might be due to the inability of bacteria associated with the sinking material to adapt to a lack of oxygen during descent. In support of this hypothesis are data from a short sediment trap deployment off Mexico. During this deployment the decrease in carbon flux between the 150 m trap and the 950 m trap was only a factor of 1.5.

Differences in the C:N:P regeneration rate ratio also appear to be associated with presence or absence of oxygen in the overlying waters. Off Mexico, where there is little if any oxygen in the overlying water, the C:N remineralization ratio was7.4, very close to the Redfield value of 6.6. Due to the lack of available oxygen to these sediments, organic-N is remineralized to NH_4 and diffuses out of the sediments without oxidation. Of Washington State, the C:N remineralization ratio was 19.8, or about 3 times Redfield. This high ratio likely results from within sediment oxidation of remineralized NH_4 to NO_3 and subsequent denitrification. Indeed, coupled nitrification-denitrification has been shown to consume approximately half of the remeneralized organic-N in these sediments (Devol and Christensen (1994).

Finally, the lack of reduced Mn and Fe in the pore waters of the Mexican coast sediments suggests either: 1) a much reduced source flux to these sediments, or 2) near complete metal mobilization and diffusive loss to the overlying waters due to lack of available oxygen for metal oxidation and reprecipitation.

Thus, it appears that the presence of the oxygen minimum zone affects the processes of early organic carbon diagenesis and elemental cycling within sediments in several significant ways: 1) it appears to increase the rain rate of reactive organic matter to the sediments, 2) it alters the C:N:P regeneration ratios, and 3) it drastically changes metal cycling.

References

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