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Zonal patterns of $\delta^{13}C$, $\delta^{15}N$ and ^{210}Po in the tropical and subtropical North Pacific

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[1] Nitrogen fixation process may supply a significant fraction of bioavailable nitrogen to surface waters, increase the oceanic sequestration of atmospheric CO_2, and alter the distribution of geochemical parameters. We report a zonal pattern of $\delta^{15}N$ and $\delta^{13}C$ in particulate organic matter (POM), and ratios of particulate ^{210}Po to dissolved ^{210}Po along a transect through the subtropical and tropical North Pacific. Both ^{15}N and ^{210}Po signals indicated an enhanced N_2 fixation in the northwestern subtropical North Pacific. The eastward decrease of N_2 fixation along this transect testified the role of aeolian Fe and P in controlling marine N_2 fixation. Associated with the zonal variations of ^{15}N and ^{210}Po, the $\delta^{13}C$ of suspended POM increased eastward, reflecting the decrease of anthropogenic CO_2 concentration in surface seawater from west to east in the study area. Our results highlight the need to examine more closely the mechanisms of possible longitudinal variation in N_2 fixation in the ocean and the role of aeolian Fe and P in controlling marine N_2 fixation and anthropogenic CO_2. **Citation:** Chen, M., L. Guo, Q. Ma, Y. Qiu, R. Zhang, E Lv, and Y. Huang (2006), Zonal patterns of $\delta^{13}C$, $\delta^{15}N$ and ^{210}Po in the tropical and subtropical North Pacific, *Geophys. Res. Lett.*, *33*, L04609, doi:10.1029/2005GL025186.

1. Introduction

[2] Nitrogen fixation is a globally important process that may supply a significant fraction of bioavailable nitrogen to surface waters, increase the oceanic sequestration of atmospheric CO_2 [*Carpenter and Romans*, 1991; *Falkowski et al.*, 1998], and at the same time alter the distribution of geochemical parameters in the ocean. The biologically mediated export of POM from the surface ocean is a crucial term in the global carbon cycle because it represents a potential long-term sink for atmospheric CO_2 [*Karl et al.*, 1997]. Organic export from the surface ocean is supported by the input of new nitrogen to the euphotic zone, including NO_3^- advecting or diffusing up from the large reservoirs of NO_3^- at depth and marine N_2 fixation by diazotrophs [*Dugdale and Goering*, 1967]. N_2 fixation and vertical NO_3^- flux from depth have different potentials for supporting primary production and affecting net removal of atmospheric CO_2. Vertical NO_3^- flux occurs with a concurrent upward flux of CO_2 and PO_4^{3-}, often close to the stoichiometric requirement of phytoplankton [*Capone et al.*, 1997]. Thus, relative to N_2 fixation, NO_3^- derived from depth has limited capacity for affecting new removal of atmospheric CO_2. N_2 fixation represents a source of new nitrogen entering the ocean that can account for a net sequestering of atmospheric CO_2 into export production if no other nutrients limit N_2 fixation [*Karl et al.*, 1997]. However, the link between N_2 fixation and anthropogenic CO_2 storage in marine environment is poorly understood.

[3] Natural ^{15}N signature of POM has been used to gain information about the nitrogen sources supporting plankton growth. The low $\delta^{15}N$ of plankton in low latitude areas was related to N_2 fixation [*Wada and Hattori*, 1976; *Karl et al.*, 1997], while in high latitudes, it was related to large isotopic fractionation during the uptake of NO_3^- [*Mino et al.*, 2002]. $\delta^{13}C$ of organic matter is also widely used as an indicator of the relative importance of marine vs. terrestrial inputs [*Sackett*, 1964] and of changes in the concentration of CO_2 in surface waters [*Quay et al.*, 1992]. ^{210}Po, a naturally occurring radioisotope that is ubiquitous in seawater, is especially enriched in proteinaceous tissues of marine organisms, and may therefore be useful as a tracer of organic carbon flux in marine systems [*Cherry and Heyraud*, 1979]. A combination of these isotope tracers will provide more detail information on marine nitrogen and carbon cycles.

[4] N_2 fixation in marine pelagic environment is latitudinal dependent and mainly restricted to tropical and subtropical oceans [*Capone et al.*, 1997]. However, little is known about the zonal patterns of N_2 fixation and its relationship to geochemical signatures in the Pacific. Here we present zonal patterns of natural ^{13}C and ^{15}N in POM and ^{210}Po along a transect from ~134°E to ~103°W in the subtropical and tropical Pacific, and their implications for N_2 fixation and its longitudinal variations.

2. Methods

[5] Surface seawaters (0~1 m) were collected along a transect from ~134°E in the northwestern North Pacific to ~103°W in the eastern tropical North Pacific during October–December 2003 (Figure 1). These stations span from the Kuroshiro Current to the North Pacific Subtropical Gyre and to the California Current. The easternmost portion of the transect is located within the Eastern Tropical North Pacific (ETNP) (Figure 1). Measurements included particulate and dissolved ^{210}Po activities and natural ^{13}C and ^{15}N abundances in POM. For ^{210}Po measurements, a 0.2 μm nitrocellulose membrane was used to separate particulate from dissolved phase. ^{210}Po

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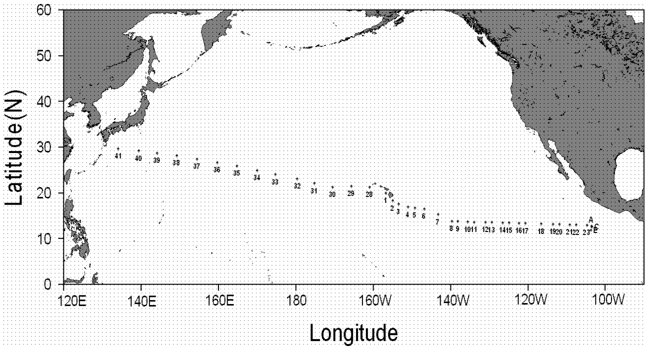

Figure 1. Sampling locations for ^{13}C, ^{15}N and ^{210}Po measurements in the North Pacific Ocean.

was auto-plated onto a silver disc and counted by alpha spectrometer with ^{209}Po as a chemical yield tracer [*Yang et al.*, 2003]. Appropriate ingrowth and decay corrections were applied to obtain the in-situ ^{210}Po activities. Reported errors were propagated from one sigma counting uncertainties. For ^{13}C and ^{15}N measurements, a total of 10 dm^3 seawater was filtered through a precombusted Whatman GF/F membrane. Isolated particulate samples were then fumed with HCl for subsequent duplicate measurements of ^{13}C and ^{15}N abundance using a Finnigan MAT DELTA^{plus} XP mass spectrometer interfaced with an elemental analyzer (Carlo Eeba NC 2500). Isotopic ratios (in terms of $\delta^{13}C$ and $\delta^{15}N$) were presented as per mil deviation from standard PDB for $\delta^{13}C$ and air N_2 for $\delta^{15}N$, respectively. Reproducibility of each measurement was within ±0.2‰.

3. Results and Discussion

[6] Values of $\delta^{15}N$ of suspended POM increased from an average of −0.1‰ (ranging from −4.1 to 3.2‰) west of 170°W to 3.2‰ (−1.3 to 8.8‰) east of 170°W (Figure 2). This isotopically light signal in the western study area was consistent with those found in areas where *Trichodesmium*, a N_2 fixing organism, is present [*Wada and Hattori*, 1976; *Saino and Hattori*, 1987; *Carpenter et al.*, 1997; *Karl et al.*, 1997]. In comparison, $\delta^{15}N$ values of suspended POM east of 170°W were close to those without the influence of N_2 fixing organism (3.3∼11‰) [*Wada and Hattori*, 1976; *Saino and Hattori*, 1987; *Carpenter et al.*, 1997]. The increase in $\delta^{15}N$ at the eastern end of our transect is likely due to the impact of denitrification in the eastern tropical North Pacific, which increase the $\delta^{15}N$ of NO_3^- at depths [*Liu and Kaplan*, 1989]. Particulate organic matter in the euphotic zone produced by utilizing the ^{15}N-enriched nitrate would have higher $\delta^{15}N$ values. The eastward increase of $\delta^{15}N$ signal in suspended POM suggests that marine N_2 fixation is more active in the northwestern subtropical North Pacific. This conclusion is consistent with previous observations that showed $\delta^{15}N$ in suspended POM at various stations in the eastern North Pacific was higher than those in the western North Pacific, attributable to the effect of N_2 fixation [*Saino and Hattori*, 1987].

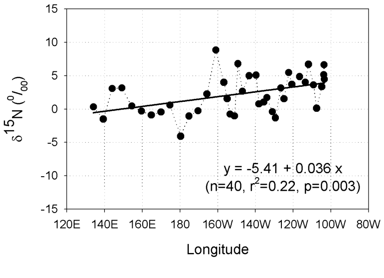

Figure 2. Variations of POM $\delta^{15}N$ values from west to east in the North Pacific Ocean.

[7] Dissolved ^{210}Po activities fluctuated around 18 dpm/100 L in surface waters, with no significant difference between the western and eastern Pacific (Figure 3a). However, particulate ^{210}Po activity, controlled by biological activities and the abundance of biogenic particles, decreased from west to east in the study area, with a relatively large fluctuation west of 170°W (Figure 3b), resulting in an eastward decrease of the ratio of particulate ^{210}Po to dissolved ^{210}Po (Figure 3c).

[8] ^{210}Po is abnormally deficient in the upper water column in oligotrophic oceans relative to productive oceans [*Kim*, 2001; *Kim and Church*, 2001]. This likely results from more rapid biological uptake of ^{210}Po and further transfer to higher trophic levels via bacteria, rather than by downward particle export [*Kim*, 2001]. Previous observations have shown a more efficient ^{210}Po uptake by bacteria than by phytoplankton (e.g., diatoms) [*Cherry and Heyraud*, 1979]. Thus, the fraction of particulate ^{210}Po in the oligotrophic ocean is higher than that in productive oceans. Indeed, a significant linear correlation between particulate ^{210}Po to

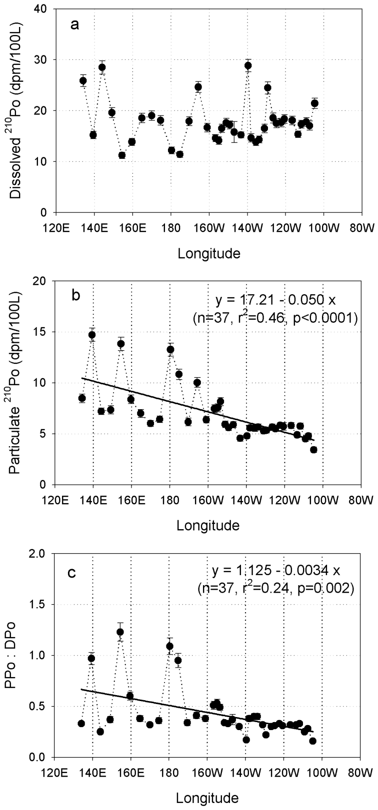

Figure 3. Longitudinal variations of (a) dissolved and (b) particulate ^{210}Po activities, and (c) the ratios of particulate ^{210}Po to dissolved ^{210}Po in the North Pacific Ocean.

dissolved ^{210}Po ratios and N_2 fixation rates by *Trichodesmium* has been reported [*Kim*, 2001], implying that ^{210}Po is a useful tracer for N_2 fixation in the ocean.

[9] The western and central North Pacific is an ecosystem dominated by cyanobacteria [*Karl et al.*, 1995], which take up ^{210}Po efficiently. Our observed westward increase of particulate ^{210}Po and the ratio of particulate to dissolved ^{210}Po indicated that compared to ETNP, the northwestern subtropical North Pacific has higher N_2 fixation rate, as also supported by the spatial variation of δ^{15}N. In fact, there exists a significant negative correlation between the particulate ^{210}Po (PPo) to dissolved ^{210}Po (DPo) ratio and δ^{15}N in the study area ($\frac{PPo}{DPo} = \frac{1}{2.09+0.28\bullet\delta^{15}N}$, with $r^2 = 0.33$ and $P = 0.0002$). The relatively large fluctuation of particulate ^{210}Po and the PPo/DPo ratios west of 170°W may result from the heterogeneous distribution of marine N_2 fixers [*Carpenter et al.*, 1993; *Zehr et al.*, 2001].

[10] The distributions of both δ^{15}N and ^{210}Po demonstrate that surface N_2 fixation is more active in the northwestern subtropical North Pacific than those in the ETNP. This geographical trend agrees well with those derived from N*, a parameter used to indicate the degree to which the nitrate concentration is in excess of that expected from the remineralization of phosphorus at stoichiometries of 16:1 [*Gruber and Sarmiento*, 1997]. N* spatial distributions in the main thermoclines showed that N* values decreased eastward in the North Pacific Ocean, indicating an enhanced N_2 fixation in the western North Pacific [*Deutsch et al.*, 2001]. The enhancement of N_2 fixation in the northwestern subtropical north Pacific coincides with the spatial variation of dissolved Fe concentration in the surface seawater. In North Pacific, the dominant input of Fe to the surface water is from aeolian dust, likely from the Gobi desert in Asia [*Duce and Tindale*, 1991] or from volcanic eruption and glaciated tilts [*Boyd et al.*, 1998]. Modeling studies of dust transport and deposition suggested that annual atmospheric Fe input to the oceans also decreased eastward in the North Pacific, giving rise to the eastward decrease of surface Fe concentrations [*Moore et al.*, 2002]. Unlike the geographical trend of dissolved Fe concentration in surface seawater, mean seasonal surface water phosphate concentration showed an increase eastward in the North Pacific [*Conkright et al.*, 2000]. The zonal patterns among ^{15}N, ^{210}Po, Fe and phosphate suggest that Fe or Fe/P may limit nitrogen fixation in the subtropical and tropical North Pacific. Recent studies suggested that P can be released from aeolian dust and N_2 fixation in the eastern tropical North Atlantic was co-limited by Fe and P [*Mills et al.*, 2004].

[11] The stable carbon isotopic composition of POM, δ^{13}C, ranged from −26.5 to −19.1‰, with an eastward increase from the subtropical to the tropical North Pacific (Figure 4). This zonal pattern can be ascribed to the effects from anthropogenic CO_2 invasion in ocean surface water [*Quay et al.*, 1992; *Cullen et al.*, 2001]. In the open ocean, phytoplankton δ^{13}C ($\delta^{13}C_p$) is a function of the stable isotopic signature of $[CO_2]_{aq}$, and the isotopic fractionation factor (ε_p) during photosynthesis. ε_p is linearly dependent on the specific growth rate, $[CO_2]_{aq}$ and a species-specific constant [*Cullen et al.*, 2001]. The penetration of anthropogenic CO_2 into the upper ocean will result in an increase in $[CO_2]_{aq}$ and a decrease of $\delta^{13}C_{aq}$ (also known as the Suess effect), and a subsequent decrease of $\delta^{13}C_p$ in the water column. This mechanism has been used to explain the discrepancy in δ^{13}C between modern POM and organic matter from deep-sea surface sediments [*Fischer et al.*, 1988].

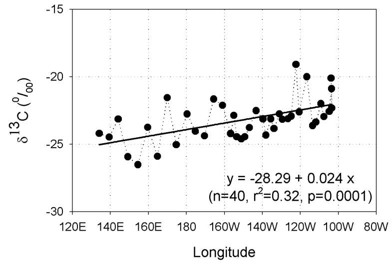

Figure 4. Longitudinal variations of POM δ^{13}C values in the North Pacific Ocean.

[12] The eastward increase of δ^{13}C of POM along the transect may thus reflect the zonal pattern of CO_2 solubility or the eastward decrease of the penetration of anthropogenic CO_2 into the upper ocean. Indeed, surface-water pCO$_2$ values increased eastward in the North Pacific [*Takahashi et al.*, 2002]. Our results here are also consistent with the spatial variation of the Revelle factor, which describes how the partial pressure of CO_2 in seawater changes for a given change in surface water DIC. The capacity for ocean waters to take up anthropogenic CO_2 from the atmosphere is inversely proportional to the value of the Revelle factor [*Sabine et al.*, 2004]. Distribution of the Revelle factor averaged for the upper 50 m water column showed an increase from west to east in the North Pacific, indicating that oceanic equilibrium concentration of anthropogenic CO_2 decreases from west to east [*Sabine et al.*, 2004].

[13] Marine N_2 fixation has direct bearing on the net capacity for the upper ocean to sequester atmospheric CO_2. In this sense, marine N_2 fixation determines the oceanic capacity to absorb excess or anthropogenic CO_2. The eastward decrease of surface N_2 fixation in the study area implies that the potential capacity to absorb anthropogenic CO_2 should decrease from west to east, inducing the eastward decrease of anthropogenic CO_2 concentration in surface water and the increase of δ^{13}C in suspended POM. Recent studies have suggested that the western North Pacific is a larger sink for anthropogenic CO_2 than previously thought [*Tsunogai et al.*, 1993]. The increased storage of anthropogenic CO_2 in the western North Pacific may possibly result from the strengthening of marine N_2 fixation in this region. However, the large POC export with interannual variability was observed in the eastern North Pacific [*Wong et al.*, 1999]. A closer examination is required for increasing understanding of the zonal variations of N_2 fixation rate, and the relationship between N_2 fixation and anthropogenic CO_2 in the North Pacific.

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