Zonal patterns of δ^{13} C, δ^{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 ²¹⁰Po to dissolved ²¹⁰Po along a transect through the subtropical and tropical North Pacific. Both ¹⁵N and ²¹⁰Po signals indicated an enhanced N₂ fixation in the northwestern subtropical North Pacific. The eastward decrease of N2 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 CO₂ 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 N2 fixation in the ocean and the role of aeolian Fe and P in controlling marine N₂ fixation and anthropogenic CO₂. Citation: Chen, M., L. Guo, Q. Ma, Y. Qiu, R. Zhang, E Lv, and Y. Huang (2006), Zonal patterns of δ^{13} C, δ^{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 CO₂ [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 CO₂ [Karl et al., 1997]. Organic export from the surface ocean is supported by the input of new nitrogen to the euphotic zone, including NO₃⁻ advecting or diffusing up from the large reservoirs of NO_3^- at depth and marine N_2 fixation by diazotrophs [Dugdale and Goering, 1967]. N₂ 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 N₂ fixation, NO₃⁻ derived from depth has limited capacity for affecting new removal of atmospheric CO_2 . N₂ 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 N₂ fixation [*Karl et al.*, 1997]. However, the link between N₂ fixation and anthropogenic CO_2 storage in marine environment is poorly understood.

[3] Natural ¹⁵N signature of POM has been used to gain information about the nitrogen sources supporting plankton growth. The low δ^{15} N of plankton in low latitude areas was related to N₂ 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]. δ^{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 CO₂ in surface waters [*Quay et al.*, 1992]. ²¹⁰Po, 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] N₂ 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 N₂ fixation and its relationship to geochemical signatures in the Pacific. Here we present zonal patterns of natural ¹³C and ¹⁵N in POM and ²¹⁰Po along a transect from ~134°E to ~103°W in the subtropical and tropical Pacific, and their implications for N₂ 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 ²¹⁰Po activities and natural ¹³C and ¹⁵N abundances in POM. For ²¹⁰Po measurements, a 0.2 μ m nitrocellulose membrane was used to separate particulate from dissolved phase. ²¹⁰Po

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

was auto-plated onto a silver disc and counted by alpha spectrometer with ²⁰⁹Po as a chemical yield tracer [*Yang et al.*, 2003]. Appropriate ingrowth and decay corrections were applied to obtain the in-situ ²¹⁰Po activities. Reported errors were propagated from one sigma counting uncertainties. For ¹³C and ¹⁵N measurements, a total of 10 dm³ seawater was filtered through a precombusted Whatman GF/F membrane. Isolated particulate samples were then fumed with HCl for subsequent duplicate measurements of ¹³C and ¹⁵N abundance using a Finnigan MAT DELTA^{plus} XP mass spectrometer interfaced with an elemental analyzer (Carlo Eeba NC 2500). Isotopic ratios (in terms of δ^{13} C and δ^{15} N) were presented as per mil deviation from standard PDB for δ^{13} C and air N₂ for δ^{15} N, respectively. Reproducibility of each measurement was within ±0.2‰.

3. Results and Discussion

[6] Values of δ^{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 N₂ fixing organism, is present [*Wada and Hattori*, 1976; *Saino and Hattori*, 1987; *Carpenter et al.*, 1997; *Karl et al.*, 1997]. In comparison, δ^{15} N values of suspended POM east of 170° W were close to those without the influence of N₂ fixing organism ($3.3 \sim 11\%$) [*Wada and Hattori*, 1976; *Saino and Hattori*, 1987; *Carpenter et al.*, 1997]. The increase in δ^{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 δ^{15} N of NO₃⁻ at depths [*Liu and Kaplan*, 1989]. Particulate organic matter in the



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

euphotic zone produced by utilizing the ¹⁵N-enriched nitrate would have higher δ^{15} N values. The eastward increase of δ^{15} N signal in suspended POM suggests that marine N₂ fixation is more active in the northwestern subtropical North Pacific. This conclusion is consistent with previous observations that showed δ^{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 N₂ fixation [*Saino and Hattori*, 1987].

[7] Dissolved ²¹⁰Po activities fluctuated around 18 dpm/ 100 L in surface waters, with no significant difference between the western and eastern Pacific (Figure 3a). However, particulate ²¹⁰Po 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 ²¹⁰Po to dissolved ²¹⁰Po (Figure 3c).

[8] ²¹⁰Po 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 ²¹⁰Po and further transfer to higher trophic levels via bacteria, rather than by downward particle export [*Kim*, 2001]. Previous observations have shown a more efficient ²¹⁰Po uptake by bacteria than by phytoplankton (e.g., diatoms) [*Cherry and Heyraud*, 1979]. Thus, the fraction of particulate ²¹⁰Po in the oligotrophic ocean is higher than that in productive oceans. Indeed, a significant linear correlation between particulate ²¹⁰Po to



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

dissolved ²¹⁰Po ratios and N₂ fixation rates by *Trichodesmium* has been reported [*Kim*, 2001], implying that ²¹⁰Po is a useful tracer for N₂ fixation in the ocean.

[9] The western and central North Pacific is an ecosystem dominated by cyanobacteria [*Karl et al.*, 1995], which take up ²¹⁰Po efficiently. Our observed westward increase of particulate ²¹⁰Po and the ratio of particulate to dissolved ²¹⁰Po indicated that compared to ETNP, the northwestern subtropical North Pacific has higher N₂ fixation rate, as also supported by the spatial variation of δ^{15} N. In fact, there exists a significant negative correlation between the particulate ²¹⁰Po (PPo) to dissolved ²¹⁰Po (DPo) ratio and δ^{15} N in the study area $(\frac{PPo}{DPo} = \frac{1}{2.09+0.28 \cdot 6^{15}N}, \text{ with } r^2 = 0.33 \text{ and } P = 0.0002$). The relatively large fluctuation of particulate ²¹⁰Po and the PPo/DPo ratios west of 170°W may result from the heterogeneous distribution of marine N₂ fixers [*Carpenter et al.*, 1993; *Zehr et al.*, 2001]. [10] The distributions of both δ^{15} N and ²¹⁰Po demonstrate

that surface N₂ 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 N₂ fixation in the western North Pacific [Deutsch et al., 2001]. The enhancement of N₂ 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 ¹⁵N, ²¹⁰Po, 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 N₂ 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 CO₂ invasion in ocean surface water [*Quay et al.*, 1992; *Cullen et al.*, 2001]. In the open ocean, phytoplankton δ^{13} C (δ^{13} C_p) is a function of the stable isotopic signature of [CO₂]_{aq}, and the isotopic fractionation factor (ε_p) during photosynthesis. ε_p is linearly dependent on the specific growth rate, [CO₂]_{aq} and a species-specific constant [*Cullen et al.*, 2001]. The penetration of anthropogenic CO₂ into the upper ocean will result in an increase in [CO₂]_{aq} and a decrease of δ^{13} C_{aq} (also known as the Suess effect), and a subsequent decrease of δ^{13} C_p in the water column. This



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

mechanism has been used to explain the discrepancy in δ^{13} C between modern POM and organic matter from deepsea surface sediments [*Fischer et al.*, 1988].

[12] The eastward increase of $\delta^{13}C$ of POM along the transect may thus reflect the zonal pattern of CO₂ 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 CO₂ 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 CO₂ decreases from west to east [Sabine et al., 2004].

[13] Marine N₂ fixation has direct bearing on the net capacity for the upper ocean to sequester atmospheric CO_2 . In this sense, marine N₂ fixation determines the oceanic capacity to absorb excess or anthropogenic CO₂. The eastward decrease of surface N2 fixation in the study area implies that the potential capacity to absorb anthropogenic CO₂ should decrease from west to east, inducing the eastward decrease of anthropogenic CO₂ 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 CO₂ than previously thought [Tsunogai et al., 1993]. The increased storage of anthropogenic CO2 in the western North Pacific may possibly result from the strengthening of marine N₂ 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 N2 fixation rate, and the relationship between N2 fixation and anthropogenic CO_2 in the North Pacific.

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