Correlation between nitrogen isotopic ratios and productivity of calcareous nannoplankton of the Quaternary sediments off Bahama Bank of the Caribbean Sea

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Calcareous nannoplankton, one of marine phytoplankton, has been used as an effective indicator for estimating not only geological age of marine sediments but also change of global marine environment, because numerical change of nanno-fossil in the sediments can be related to palaeoclimatologic cycles such as Milankovitch one. This suggests that the productivity of nannoplankton in marine is controlled by change of nitrate content in photic zone caused by that of upwelling intensity. Therefore, it can be expected that numerical change of such phytoplankton is related directly to $\delta^{15}N_{air}$ values of marine sediments because of isotopic fractionation in consumption process of nitrate as a nutritive by nannoplankton. In spite of its importance, such studies have been not reported.

We measured $\delta^{15}N_{air}$ values of marine sediments (nanno chalk) and the number of nannofossil in them in a period of 300 ka to 1800 ka at intervals of 5 ky to 10 ky, using the core samples from ODP Hole 1006A drilled off Great Bahama Bank of the Caribbean Sea. We found that there are clearly positive correlations between $\delta^{15}N_{air}$ value, productivity of nannoplankton and foraminiferal $\delta^{18}O_{PDB}$ value. As expected, the larger the number of nannofossil, the higher the $\delta^{15}N_{air}$ value become. Their $\delta^{15}N_{air}$ values fluctuate in a range of +0.1 ‰ to +5.8 ‰, giving the mean value of +2.9 ‰. This fluctuation shows a cycle per 100 ky agreeing with Milankovitch cycle found for changes of foraminiferal $\delta^{18}O_{PDB}$ value (*Globigerinoides ruber*) and the number of nannofossil in the same core. It has been known that in the interglacial climate foraminiferal $\delta^{18}O_{PDB}$ values in marine sediments become low and in the glacial one their values become high. Therefore, our results indicate that the changes of $\delta^{15}N_{air}$ values of marine sediments may be related to the difference in productivities of nannoplankton controlled by changes of palaeoclimate having an effect on the intensities of upwellings in the Bahama Bank area. The changes of intensities of local winds on the earth control those of upwellings in the local area causing numerical changes of planktons such as nannoplankton and diatom and changes of $\delta^{15}N_{air}$ values of marine sediments. Therefore, it can be expected that we can obtain the information about the global atmospheric dynamics during the Quaternary by clarifying the changes of $\delta^{15}N_{air}$ values and numbers of nannofossil and diatom of core samples of marine sediments from all over the world.

Determination of iron(III)-complexing ligands originated from marine phytoplankton using cathodic stripping voltammetry

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Dissolved iron in the oceans is overwhelmingly bound to strong organic ligands that may be produced by microorganisms (Macrellis et al. 2001). Several prokaryotic species such as cyanobacteria and heterotrophic bacteria release low molecular weight ligands with high affinity for iron (siderophores) and facilitate the iron uptake. On the other hand, certain eukaryotic phytoplankton also releases iron(III)-complexing ligands although the biochemical role of these chelates is unknown (Boye and van den Berg 2000). Here we discuss the iron(III)-complexing ligands in laboratory cultures of coastal marine phytoplankton.

The ligands were separated and concentrated by solid-phase extraction with a Sep-Pac C18 cartridge column, and determined by adsorptive cathodic stripping voltammetry with competitive ligand equilibration (CLE/ACSV). For the determination of the ligands, this method provided more accurate values than CLE/ACSV without the solid-phase extraction. Various cartridges for the solid-phase extraction were tested for retention capacity with two bacterial siderophores, desferrioxamine B and rhodotorulic acid. A series of cartridges with hydrophobic packing were more effective with retention of the ligands, which is in agreement with previous results (Macrellis et al. 2001).

The extracted compounds from *Rhodomonas ovalis* (Cryptophyceae) cultures showed iron(III)-binding affinities by the electrochemical analyses. Furthermore, higher amounts of the ligands was produced under iron-limited but relatively-high-iron conditions. Some results of other coastal phytoplankton are described, which suggest the excretion of iron(III)-binding ligands depends on species of phytoplankton and iron concentrations in the grown cultures.

References

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