

ASSESSMENT OF MICROBIAL ALTERATION IN MARINE SEDIMENTS: EVIDENCE FROM COMPOUND-SPECIFIC ISOTOPE ANALYSIS OF AMINO ACIDS

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Sediment core samples have widely been used to reconstruct paleoenvironments by applying bulk isotope analysis of carbon and nitrogen contained as well as molecular isotope analysis of lipid biomarkers preserved in sediments. On the other hand, applications of compound-specific isotope analysis of amino acids (CSIA-AA) are still in the stage of development for sediment samples, and we expect that the CSIA-AA can provide information of nitrogen cycle in paleoenvironments. However, because amino acids are high bioavailable organic compounds in biosphere, the isotopic compositions (e.g., $\delta^{15}N$) of them could be easily and rapidly altered during diagenesis (i.e., degradation), recycle, and re-production in sediments. Therefore, knowing alteration of the isotopic compositions in sediments is essential to apply the CSIA-AA in geochemical studies. So far, although several parameters such as DI (using concentration of AAs, Dauwe et al., 1999) and $\sum V$ (using the $\delta^{15}N$ values of trophic AAs, McCarthy et al., 2007) were used to see the microbial degradation in sediments, the linkage between molar and isotopic compositions is still unclear. In this study, based on CSIA-AA, we suggest a new microbial degradation index to assess microbial alteration in marine sediments.

We analysed molar abundance and the $\delta^{15}N$ values of amino acids in a sediment core collected from the Central Yellow Sea and in surface sediments from seven different locations. Each of sediment sample (0.5~1.5g dry weight) was hydrolysed and defatted. After the dryness, amino acids were purified with a cation-exchange column (Takano et al., 2010). the purified amino acids were derivatized to N-pivaloyl-isopropanol (NPIP) esters for GC-MS, GC-FID, and GC-C-IRMS analyses.

In the core sediments, decrease in the AA concentration and increase in the $\delta^{15}N_{AAs}$ value are found with depth of the core, but there are in different patterns at level of individual AAs (*Figure 1*). For instance, phenylalanine is considerably enriched in ¹⁵N by 1.8~3.9‰ in the surface sediments, with the high degradation rate by 80~90%, whereas the its concentration and the $\delta^{15}N$ values are likely constant below 2 cm of the seafloor. Interestingly, glycine is the most susceptible AA with microbial degradation, representing the highest enrichment in ¹⁵N by 7.1‰ even with a small degradation rate and is remained large proportion (c.a. 30%) in the sediments. Although both DI and ΣV parameters basically reflect microbial degradation with enrichment in ¹⁵N through the core, a poor correlation (r²=0.15) is always observed between DI and ΣV . That is probably because both parameters are estimated by a single factor: mol % for the DI, $\delta^{15}N$ for the ΣV values, respectively. However, in perspective of geochemistry, AAs are involved in many processes such as assimilation, degradation, and re-production. Moreover, the transformation of AAs during the utilizations generally accompanies with isotopic fractionation. Thus, both molar and isotope compositions of AAs are required for interpretation of nitrogen cycle.



Based on these results, we suggest a new microbial degradation index using two AAs (i.e., glycine and phenylalanine), which is defined as (mol % * δ^{15} N)_{phenylalanine-glycine} for combining the AAs proportion relative to total hydrolyzable amino acids (THAAs) and the δ^{15} N values. In this new parameter, the degree of microbial degradation is enhanced with the increase of differences of (mol % * δ^{15} N) between glycine and phenylalanine, which basically correlates (r²=0.53) with the degradation index (DI) but has a high sensitivity through core sediments. Thus, we conclude that microbial activity causes a considerable alteration on the δ^{15} N values of glycine, resulting in of bulk with depth in sediments.



Figure 1. Vertical profile (concentration and nitrogen isotope ratio) of THAA, glycine, and phenylalanine, as well as degradation and (mol $\% * \delta^{15}N$)_{phenylalanine-glycine} indexes in the core YSPOL D10 collected from the Central Yellow Sea. Mol%, mean, and standard deviation used for the estimation of DI are calculated according to the equations in Dauwe et al (1999). ΣV values were estimated according to the equations in McCarthy et al (2007).

References

- 1. DAUWE, B., MIDDELBURG, J. J., HERMAN, P. M. & HEIP, C. H. 1999. Linking diagenetic alteration of amino acids and bulk organic matter reactivity. *Limnology and Oceanography*, 44, 1809-1814.
- 2. MCCARTHY, M. D., BENNER, R., LEE, C. & FOGEL, M. L. 2007. Amino acid nitrogen isotopic fractionation patterns as indicators of heterotrophy in plankton, particulate, and dissolved organic matter. Geochimica et Cosmochimica Acta, 71, 4727-4744.
- TAKANO, Y., KASHIYAMA, Y., OGAWA, N. O., CHIKARAISHI, Y. & OHKOUCHI, N. 2010. Isolation and desalting with cation - exchange chromatography for compound - specific nitrogen isotope analysis of amino acids: application to biogeochemical samples. Rapid Communications in Mass Spectrometry, 24, 2317-2323.