Long-chain alkenediones found from marine sediments and their unsaturation ratios: key compounds to study the evolution of alkenone biosynthetic pathway?

*Satoshi Furota[1], Hideto Nakamura[2], Ken Sawada[3]

1. Department of Biogeochemistry, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2. Faculty of Science, Osaka City University, 3. Department of Earth and Planetary Sciences, Faculty of Science, Hokkaido University

Long-chain alkenones (C_{37} to C_{39} alkenones) are characteristic compounds produced by haptophyte, and their unsaturation ratios in marine sediments have been used as a proxy for sea surface temperature (SST). Paleocenographic studies using the alkenone proxies are based on the physiological features of the modern alkenone producers such as *Emiliania huxleyi* and *Gephyrocapsa oceanica*. However, these species firstly occurred at ca. 0.29 Ma and ca. 1.85 Ma, respectively, and thus, understandings of the evolutional variations in the alkenone biosynthetic pathway is important to apply the alkenone proxies to the older age. In our recent study, $C_{38:2}$ alkenedione was found in the Miocene to Pliocene marine sediments (Furota et al., 2016). This compound was interpreted to be produced by ancient alkenone producers, because (1) the molecular structure resembles to those of the alkenones, (2) it has not been detected from the extant alkenone producers and sediments, and (3) the relative abundance of the alkenedione to alkenones were significantly higher in the older sediments. Therefore, the alkenedione presumably is a key compound to study the evolutional changes in the biosynthetic pathway of alkenones.
We analyzed the alkenones and alkenediones in the hemipelagic sediments recovered from the NE Atlantic during the IODP exp. 339 to evaluate the variations in their compositions at 100,000-year scale from the late Miocene to Pleistocene. We measured using gas chromatography–flame ionization detector (GC–FID) and GC–mass spectrometry (GC–MS) equipping with a mid-polarity capillary column (VF-200 ms). The GC analysis using the mid-polarity column makes the peak shapes sharp and achieves the well chromatographic separations in the analyses of long-chain alkenones, and thus, several recent studies applied this technique (Longo et al., 2013; Furota et al., 2016).
The long-chain alkenones and the C_{38} alkenediones were detected from all the study samples. Interestingly, the carbon numbers of the alkenediones are only C_{38} in contrast to the alkenones. Mass fragmentogram shows that the C_{38} alkenedione has a methyl-ketone and ethyl-ketone groups at the each terminals of the carbon chain. In addition to $C_{38:2}$ alkenedione as reported previously, we firstly identified tri-unsaturated ($C_{38:3}$) alkenedione in the late Pliocene–Pleistocene sediments.
The relative abundances of the C_{38} alkenediones to alkenones were significantly higher in older sediments, and gradually decreased from the Miocene to Pleistocene. These results support the interpretation that the alkenediones could be produced by the ancient alkenone producers, and imply that those producers decreased from the Miocene to Pleistocene. The unsaturation ratios of C_{38} alkenediones, defines as $C_{38:2}/(C_{38:2} + C_{38:3})$, highly correlate with the unsaturation ratios of the C_{37} alkenones ($U^{K'}_{37}$) ($R^2 = 0.85$). This fact strongly suggests that the alkenediones had a similar biological function and biosynthetic pathway related to the alkenones. Furthermore, the carbon number of alkenediones (C_{38}) is averaged one for those of alkenones (C_{37}–C_{39}), and the positions of ketone groups are equal to those of alkenones. From these results, we conclude that the C_{38} alkenedione had the similar functions with the alkenones, and might be produced by primitive alkenone biosynthetic pathway.

References

Furota et al. (2016) Org. Geochem. 101, 166–175.

Longo et al. (2013) Org. Geochem. 65, 94-102.

Keywords: Alkenone, Alkenedione, Paleoceanography

