Discovery of alkenones with variable methylene interrupted double bonds in *Emiliania huxleyi*: Implications for biosynthetic pathways

YINSUI ZHENG[1,2], JAMES T. DILLON[1], YIFAN ZHANG[1], YONGSONG HUANG[1]*

[1] Brown Univeristy, Providence, RI, USA 02912 (*correspondence: yongsong_huang@brown.edu)

[2] Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543 (yinsui_zheng@brown.edu)

Alkenones (C_{37} to C_{40}) are highly specific biomarkers produced by certain haptophyte algae in ocean and lacustrine environments and have been widely used for paleoclimate studies. Unusual shorter-chain alkenones (e.g. C_{35} and C_{36}) have been found in environmental and culture samples but the origin and structures of these compounds are much less understood. The marine alkenone producer, *Emiliania huxleyi* CCMP2758 strain (a mutant of the benchmark strain NEPCC55a that was used to establish the widely cited, culture-based ocean alkenone temperature calibration) was reported with abundant $C_{35:2}$Me ($\Delta^{12,\ 19}$) alkenone when cultured at 15 °C [1]. Here we show, when this strain is cultured at 4 to 10 °C, CCMP2758 produces abundant $C_{35:3}$Me, $C_{36:3}$Me and small amount of $C_{36:3}$Et alkenones with unusual double bond positions of $\Delta^{7,\ 12,\ 19}$. We determine the double bond positions of the $C_{35:3}$Me and $C_{36:3}$Me alkenones by GC-MS analysis of the dimethyl disulfide and cyclobutylimine derivatives, and provide the first temperature calibrations based on the unsaturation ratios of the C_{35} and C_{36} alkenones. Previous studies have found $C_{35:2}$Me ($\Delta^{14,\ 19}$) and $C_{36:2}$Et ($\Delta^{14,\ 19}$) alkenones with three-methylene interruption in the Black Sea sediment, but this is the first reported instance of alkenones with a mixed three and five-methylene interruption configuration in the double bond positions. The discovery of these alkenones allows us to propose a novel biosynthetic scheme, termed shorter-chain alkenone (SCA) biosynthesis pathway that simultaneously rationalizes the formation of both the $C_{35:3}$Me ($\Delta^{7,\ 12,\ 19}$) alkenone in our culture and the $\Delta^{14,\ 19}$ alkenones in the Black Sea type alkenones without invoking new desaturases for the unusual double bond positions. In this presentation, we will also discuss a new alkenone unsaturation index, $U^{K''}$ for lacustrine haptophyte species [2].

[1] Prahl *et al*. (2006) *Geochim. Cosmochim. Acta* **70**, 2856–2867. [2] Zheng *et al*. (2016) *Geochim. Cosmochim. Acta* **175**, 36–46