SIMULTANEOUS GAS CHROMATOGRAPHIC ANALYSIS OF LONG CHAIN ALKENONES AND ALKENOATES

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Introduction

Long chain alkenones (LCAs) have been widely used for reconstructing paleotemperatures for over 30 years (Herbert, 2001; and references therein). Long chain Esters/Alkenoates (LCEs) are unsaturated fatty acid methyl and ethyl esters produced by haptophyte algae alongside LCAs, and are known to also display strong temperature sensitivity. Unfortunately, the conventional Gas Chromatography (GC) method using non-polar GC stationary phase generally does not resolve LCEs from LCAs. Instead, partial and even full co-elution occurs (e.g., Nakamura et al., 2014). Thus, the standard procedure for alkenone analysis includes an initial step to remove the LCEs by saponification (e.g., Jaraula et al., 2010). As a result, paleotemperature proxies based on LCEs or combined LCEs and LCAs have gained little applications (Conte et al., 1992). This study is aimed at eliminating the analytical hurdles for applications of LCE-based paleothermeters, as well as improving peak resolution of LCAs.

Results

We selected culture and sediment samples from three different groups of haptophytes to demonstrate the separation of LCAs and LCEs using different gas chromatographic methods. It is for the first time that the alkenones and alkenoates can be simultaneously analyzed without any further cleanup or derivative reactions by using Rrx200-R method (Figure 1). This is important for several reasons: (1) It greatly simplifies the procedure for alkenone-based paleotemperature reconstructions by avoiding saponification step. Saponification not only lengthens sample preparation but also can cause significant loss of target alkenones; (2) It permits the methyl and ethyl alkenoates to be quantified and calibrated against temperature separately. Without using Rtx-200 column, the alkenoates may still be chemically recovered after saponification and methylated for GC analysis. However, this approach would combine the methyl and ethyl alkenoates and removes potentially valuable information from individual methyl and ethyl alkenoates; (3) Our previously proposed VF-200 ms column (Longo et al., 2013) does not separate $C_{36:2}$OEt from $C_{37:4}$Me. This is dangerous for paleotemperature reconstructions because the $C_{36:2}$OEt can be misidentified as $C_{37:4}$Me without saponification, resulting in abnormally low temperatures using U^{K}_{37} or $U^{K''}_{37}$ indices; (4) The use of Rtx200-R method not only improves the separation between LCAs and LCEs, but also greatly enhances the resolution among LCA peaks including LCA isomers. This will prompt the application of U^{K}_{38Me} and U^{K}_{38Et}.

Conclusions

Rtx-200 column allows simultaneous analysis of LCAs and LCEs with baseline resolution. This new GC method greatly simplifies and shortens the analytical procedure for alkenones and alkenoates by removing saponification step and associated compound loss. Methyl and ethyl alkenoates can now be routinely and independently analyzed alongside alkenones to provide new paleoclimate information.

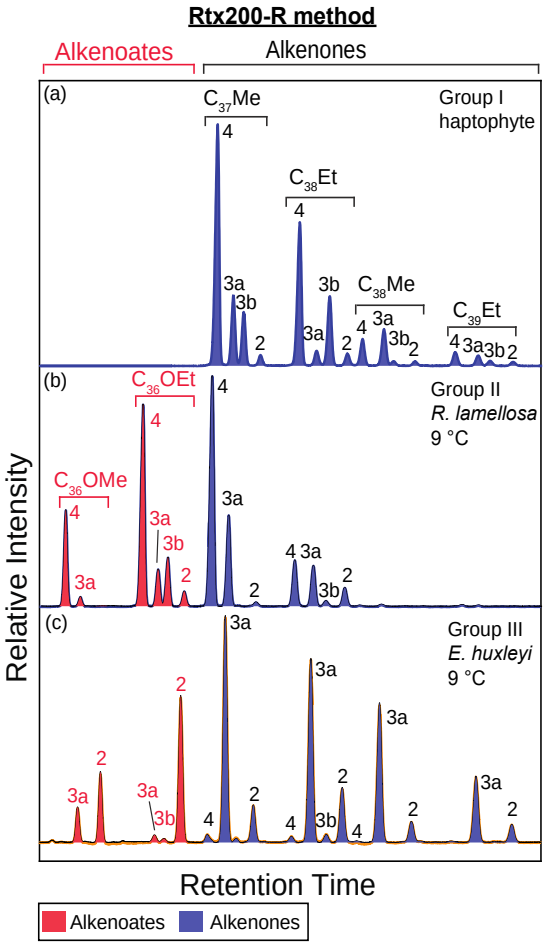

Figure 1 *Gas chromatographic separation of LCAs and LCEs from Group I haptophyte (Greenland sediment, a), Group II haptophyte (R. lamellose, b) and Group III haptophyte (E. huxleyi, c) using Restek Rtx-200 column. LCE peaks are filled in red and LCAs in blue. The double bond numbers of LCAs/LCEs are labeled on top of the peaks.*

References

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