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Alkenone purification for hydrogen isotope analysis by HPLC-MS: implications for paleoenvironmental reconstruction

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Compound-specific hydrogen isotope analysis of individual alkenones has not been possible due to chromatographic coelution of the alkenones with the same carbon chain length and different degrees of unsaturation. Consequently, previous paleoenvironmental studies reported the δD values of a mixture of coeluting alkenones (e.g., Englebrecht and Sachs, 2005; Schouten et al., 2006). Here, we present a semi-preparative Normal Phase High Performance Liquid Chromatography- Mass Spectrometry (NP-HPLC-MS) method for purifying long-chain (C_{37} and C_{38}) unsaturated methyl and ethyl ketones (alkenones) on the basis of chain length and degree of unsaturation. This method has been developed to minimize sample handling and maximize recovery so that compound-specific hydrogen isotope analyses can be performed on alkenone-lean samples. Measurements of δD values across individual HPLC peaks of standards and the $C_{37:3}$ alkenone demonstrate the necessity of collecting at least 92% of the peak in order to maintain isotopic integrity.

This method was applied to purify alkenones in suspended particles and surface sediments collected along the salinity (0 to 3.8 PSU) and water δD (-56.8 to -3.8 per mil VSMOW) gradient of the Chesapeake Bay in Maryland and Virginia, eastern United States. Hydrogen isotopic compositions of tri- and di-unsaturated C_{37} and C_{38} alkenones differed significantly on the basis of chain length and the degree of unsaturation demonstrating the importance of GC/IRMS analyses of individual alkenones for accurate paleoenvironmental reconstructions. A positive linear correlation was ob-

served between water and individual alkenone δD values along the Bay. Fractionation factors between individual alkenones and water remained constant along the salinity gradient of the Bay with $\alpha_{C37:3-H2O}$ = 0.826, $\alpha_{C37:2-H2O}$ = 0.849, $\alpha_{C38:3-H2O}$ = 0.817, and $\alpha_{C38:2-H2O}$ = 0.835. This suggests either that salinity doesn't significantly affect the hydrogen isotope composition of individual alkenones in the Chesapeake Bay, which would contradict the culturing study of Schouten et al. (2006), or that there is a change in the population of alkenone producers along the salinity gradient (e.g., *G. oceanica* to *E. huxleyi*), with the D/H fractionation imparted to alkenones being just different enough to cancel the effect of salinity. Schouten et al. (2006) did observe fractionation factors of cultured alkenones from *G. oceanica* that were about 0.025 units ($\sim$25 per mil) greater than those from *E. huxleyi*.

Constant fractionation factors between alkenones with different chain lengths but the same degree of unsaturation ($\alpha_{C37:2-C38:2}$and $\alpha_{C37:3-C38:3}$ = 1.01), and those with the same chain length but different degrees of unsaturation ($\alpha_{C37:2-C37:3}$and $\alpha_{C38:2-C38:3}$ =0.97) in all samples suggest that these values may represent hydrogen isotope fractionation associated with elongation and desaturation during alkenone biosynthesis. If so, a mass balance calculation indicates that hydrogen from NADPH-the presumed reductant during chain elongation-has a δD value of -390 per mil.

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