Biogeosciences Discuss., 6, C725–C729, 2009
www.biogeosciences-discuss.net/6/C725/2009/

Biogeosciences Discussions

Interactive comment on "Growth phase dependent hydrogen isotopic fractionation in alkenone-producing haptophytes" *by* M. D. Wolhowe et al.

Anonymous Referee #1

Received and published: 16 June 2009

Review of Wolhowe et al - Biogeosciences The manuscript presents interesting data on the hydrogen isotopic composition of C37 alkenones (δDK37s) from batch culture experiments with Emiliania huxleyi and Gephyrocapsa oceanic exhibiting benefits and impeding factors for their application in paleosalinity studies and focusing on their use as a proxy for non-thermal physiological stress impacts on the UK'37 paleotemperature index. The authors' main findings are:

1) The confirmation of an isotopic offset between di- and tri-unsaturated C37 alkenones as previously reported in D'Andrea et al., (2007) and Schwab & Sachs (2009).

2) This offset appears to be constant with growth stage and suggests the existence

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

of a single, well-defined value which the authors propose to allow the accurate determination of δD values for individual alkenones by means of an isotope mass balance approach that would avoid chemical separations of individual alkenones.

3) The observation of changes in the isotopic fractionation between growth medium and C37 alkenones in certain growth stages and nutrient availability. This finding is suggested to serve as objective tool to identify and correct the effect of nutrient stress on UK'37 temperature records.

The paper is well composed, initially reviewing the fundamentals of alkenones δD values for their use as paleoclimate proxies to reconstruct water composition and physiological stress as well as associated analytical concerns. The results of the manuscript would be interesting for the community of scientists using or interpreting hydrogen isotope ratios in lipids in the biogeosciences and paleoclimatology. I would like to suggest that the manuscript be accepted for publication after several issues discussed below are dealt with.

I have several concerns regarding the application of alkenone δD values in order to assess the effect of nutrient stress. It should be noted that the authors failed to refer to the latest findings by Zhang et al. (2009) where the effect of nutrient limitation and growth rate on D/H fractionation in marine and freshwater algal lipids was investigated. Based on their results the findings of Wolhowe et al. are contradictory. Wolhowe et al. generally observe greater D/H fractionation under nutrient limitation whereas Zhang et al. (2009) observed less D/H fractionation under nutrient limitation, particularly in isoprenoid (branched) lipids. Wolhowe et al. ought to consider and comment on these opposed datasets as well as additionally include the findings in Zhang et al. (2009) regarding the possible temperature effect on D/H fractionation.

Regarding the authors' analytical concerns in association with differing dD values for different alkenones, they should refer to Schwab & Sachs (2009). There it was shown that with a collection of at least 92% of the individual alkenone peak from an HPLC the

BGD

6, C725–C729, 2009

isotopic integrity is assured. They present the purification methodological approach using a semi-preparative normal-phase high-performance liquid chromatography-mass spectrometry method (NP-HPLC-MS) providing reliable isotopic values for the individual alkenones. In addition, they propose to use the lack of co-variation between the unsaturation ratio and the combined alkenone δD values as a criterion to assess the extent to which changes in proportions of alkenones of different degrees of unsaturation caused changes in the combined alkenone δD values. The authors ought to consider this relevant study when discussing the implications of their data for the interpretation of alkenone D/H data in paleoclimate reconstructions.

Additional issues:

1) The δD values of individual alkenones as a potential proxy for stress in paleoceanographic studies should be better justified. Besides the stress, δD values of alkenones are also affected by other factors, such as the isotope composition of water for the biosynthesis, as shown by Englebrecht and Sachs (2005). Interpretation of δD records of alkenones must take all factors into consideration. Moreover, the batch experiments of different growth stages by limiting nutrient supply may not reflect the growth conditions of the alkenone-producing haptophytes in the ocean. If the ocean sediment does preserve the stress signal, as the authors suggest, it implies that sedimentary alkenones derived from cells in the exponential stage of growth. Is this reasonable? What fraction of sedimentary alkenones may actually derive from senescent cells, or cells in the stationary phase of growthâĂŤa state most often caused by nutrient-depletion itself?

2) The authors did not clearly address the Uk'37 difference of 0.15 between their experiment and Prahl et al (1988) at the same temperature (15°C). They mentioned that this was an inherent property of their working stock E. huxleyi, which begs for additional explanation.

3) The authors should justify the error produced by their mass-balance calculation of

BGD
6, C725–C729, 2009

δD values of individual alkenones. The error of the inclusion of a, Uk'37, measured δDK37s in the equation should be addressed as none of the three parameters is perfectly constrained.

4) The authors claimed that the measured enriched D/H ratios of K37:3 is an analytical artifact of the argentation chromatography based on the K37:3 recovery. The authors should address why the K37:3 had higher recovery in stationary phase samples, but lower in exponential phase samples.

5) The authors stated (with respect to the G. oceanica culture water), "variability in αk37-water is driven largely by variability in δDK37 values ". This is not entirely correct. The changes in δDwater also significantly affect αk37-water. Assuming δDK37s = -200 ‰ and δDwater changes from 2 to -18‰ then αk37-water would change from 0.7984 to 0.8147 (a non-trivial difference of 0.0163). If, on the other hand, δDK37s changed from -200 to -180‰ and δDwater was 2‰ then αk37-water would change from 0.8184 to 0.7984 (a difference of 0.01996).

6) The authors state "the growth-phase effect on αk37-water is not hapophyte species-specific", as they claimed they observed "a similar offset between exponential and stationary phase". However, the αk37-water offset between exponential and stationary phase shown in Fig. 4 does not support this statement.

7) The authors should cite oneor more studies on pg. 5 when they state "the alkenones reflect the exponential dividing cells".

8) Apparent calculation errors:

a) P.4: δDwater change induced by open ocean salinity (32-37), δD should range from 2-22‰ not 1-21‰ $thetranslated\delta$DK37s would be -208 to -193, not -209 to -193.

b) P.9: the precision of δDK37 ($\pm$3-5‰ corresponds to an uncertainty in salinity of 0.75-1.25 units, not $\pm$1.5 units.

c) P.18: if δDwater =-5.9, δDK37s = -188.8, αk37-water = 0.816, not 0.817. The authors

BGD
6, C725–C729, 2009

should also clarify the uncertainty is standard deviation, or the maximum difference at various situations. If the uncertainty is standard deviation, the number should be 0.006; If the uncertainty is maximum difference at various situations, the number should 0.007, not 0.005 as in the text. The same questions goes for the stationary phase αk37-water.

d) P.18: make the numbers consistent for text and figures (Fig.3).

e) P.22: The average exponential-phase values of δDK37:2 (-175.0) and δDK37:3 (-198.1), and Uk37' = 0.4, would produce δDK37s =188.9 and αk37-water of 0.816, not δDK37s = -186 and αk37-water =0.819. If Uk37' shifted to 0.3, δDK37s would be -191.2, αk37-water =0.814, not δDK37s = -189, αk37-water = 0.816.

Interactive comment on Biogeosciences Discuss., 6, 4165, 2009.