INTRODUCTION

Long-chain alkenones have been widely used by paleoceanographers to reconstruct sea surface temperatures\(^1\), and in the last decade, hydrogen isotope ratios of long-chain alkenones (\(\delta^2H_{\text{C37}}\)) have been explored as a proxy to reconstruct sea surface salinities in the geologic record\(^2,3\). The \(\delta^2H_{\text{C37}}\) ratios likely reflect growth water \(\delta^2H_{\text{C37}}\) ratios and salinity, as shown in batch and continuous cultures\(^4,5,6\). Alkenones are synthesized solely by select species of haptophyte algae, which are genetically divided into three groups\(^7\), and each have characteristic alkenone distributions\(^8\). The three groups of alkenone producers also each have preferred environmental niches that correspond to specific salinity ranges. Group I haptophytes are found in lacustrine environments, and synthesize tri-unsaturated isomers with chain lengths of 37 – 39\(^8\). Group II haptophytes are present in oligohaline, marginal marine, and hypersaline lakes, and do not create tri-unsaturated isomers, but are the probable producers of the C\(_{35}\) and C\(_{36}\) alkenones. Group III haptophytes are open marine species, which generally synthesize alkenones with chain lengths from 37 – 39 and also do not create tri-unsaturated isomers, but are the probable producers of the C\(_{35}\) and C\(_{36}\) alkenones. Group II (marginal marine) and Group III (open marine) species have been shown to have distinct \(\delta^2H_{\text{C37}}\) ratios, with Group II being more isotopically enriched than Group III\(^9\). Previous studies have shown that all three groups contribute alkenones to the sedimentary record in the Baltic Sea\(^10\). Examining alkenone distributions and their hydrogen isotope ratios in a sediment core from the Baltic Sea could thus be used to disentangle the signals of the different haptophyte groups.

Results

Here we investigate alkenone distributions and \(\delta^2H_{\text{C37}}\) ratios in a down-core record from the Arkona Basin in the Baltic Sea. The present day Baltic Sea is a setting with a large salinity gradient due to an open connection with the North Sea, creating different niches for haptophyte species adjusted to specific salinities and allowing for mixing between alkenones from marine and coastal species that end up in the sedimentary record.

Shifts in distribution and presence / absence of certain individual alkenones change along with phase transitions in the Baltic Sea (Figure 1). The freshwater Ancylus Lake phase is characterized by tri-unsaturated isomers, indicating the presence of Group I producers. The higher salinity Littorina Sea phase does not contain any tri-unsaturated isomers, but does contain C\(_{35:2}\) and C\(_{36:2}\), which indicate that Group II producers likely dominate this phase. The Modern Baltic phase is characterized by a mixed Group II and III signal. We observe two major shifts in \(\delta^2H_{\text{C37}}\) ratios down-core. One shift occurs in the middle of the low salinity Ancylus Lake phase, and the other is at the boundary between the Littorina Sea and Modern Baltic Phase. The second shift is a depletion of approximately 25 \(\%\), and coincides with a shift in alkenone distribution, leading to the conclusion that this is most likely the result of a species change. The mid-Ancylus Lake shift is an enrichment in \(^2\text{H}\) of around 50 \(\%\), and does not correspond to a change in alkenone distribution. The timing of this isotope change aligns...
with a diminished Scandinavian ice sheet\textsuperscript{11} and is most likely representing a shift in source water from isotopically light ice melt to precipitation dominated source with a relatively heavy isotope ratio.

Conclusions

Because the presence and absence of certain alkenones and isomers coincides with different environmental conditions, mainly shifts in salinity, the occurrence of these alkenones can be used to better understand past salinity changes in other marginal marine environments. In the Baltic Sea, $\delta^2H_{C_{37}}$ ratios are sensitive to both changes in species and source water. Alkenone distributions, can help interpret $\delta^2H_{C_{37}}$ ratios in light of changes in salinity as well as species composition.

![Figure 1 Alkenone distribution in the Arkona Basin over the last 10.6 ka with hydrogen isotope ratios of the combined $C_{37}$ alkenones measured on the same samples. A ~50 $\%_o$ shift is noted in the middle of the Ancylus Lake phase and does not align with any distribution changes, implying that species are not the cause of the significant isotopic enrichments. The 25 $\%_o$ shift from the Littorina Sea phase into the Modern Baltic phase (M.B.) coincides with a shift in alkenone distribution, suggesting that a shift in species is responsible for the change in isotopes.](image)

References

3Kasper et al. (2014). Climate of the Past 10, 251 – 260.