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Variations in carbon isotope composition of microfossils and bulk organic matter from the Middle Ordovician through Wenlock (Silurian) in Estonia

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Variations in carbon stable isotopes help to identify and interpret changes in carbon cycling, climate, environmental conditions and biosphere. The Ordovician and Silurian succession of Baltoscandia has become a model area for studying carbon isotope composition of carbonate rocks ($\delta^{13}C_{carb}$), but less is known about the composition of organic matter ($\delta^{13}C_{org}$). Yet comparison of changes in different carbon reservoirs is crucial for a better understanding of isotopic events and past carbon cycle in general. Often the $\delta^{13}C_{org}$ trends are more variable than the $\delta^{13}C_{carb}$ curves, and to some extent this may be attributed to a mixture of different sources of organic matter. Lécuyer and Paris (1997) proved that the isotopic composition of organic matter of different microfossil groups (palynomorphs) may be rather different. Vandenbroucke *et al.* (2013) studied this aspect further based on data across the Silurian Ireviken Event interval on Gotland, Sweden. They showed that palynomorph $\delta^{13}C_{org}$ values are lower than the corresponding bulk organic matter values, and that scolecodonts (jaws of benthic polychaete worms) are systematically *c*. 0.6‰ lighter than the planktonic chitinozoans. This somewhat unexpected pattern was interpreted to be a function of trophic state, infaunal mode of life of the polychaetes and changes in primary productivity (Vandenbroucke *et al*. 2013). In this study we aim to examine whether similar trends occur in other localities and stratigraphic levels and provide new insights for interpreting the variations in carbon isotope composition in the Early Palaeozoic.

We collected 18 limestone and marl samples from the mid-Ordovician to Wenlock succession of the Lelle and Paatsalu cores (central Estonia) and Uuga cliff (NW Estonia), generally one sample per one Baltic regional stage. All samples were dissolved in HCl and organic-walled microfossils were hand-picked for isotope analysis, separating different groups into different containers. In most samples the palynomorph assemblage was dominated by chitinozoans and scolecodonts, but prasinophycean algae, graptolite fragments, hydroids and kukersite kerogen aggregates were also encountered at some levels. Acritarchs were abundant, but too small to be selectively hand-picked in sufficient numbers for mass-spectrometry. From the same samples, carbon isotope composition of different palynomorph groups and bulk organic matter was measured. In few samples one of the main groups turned to provide insufficient material for the analysis. In order to provide a high-resolution chemostratigraphic background and establish new reference sections for central Estonia, *c*. 400 bulk carbonate samples were analysed for $\delta^{13}C_{carb}$ from the Lelle and Paatsalu cores. The main isotopic excursions known from elsewhere in the region were identified in these sections, including the Mid-Darriwilian (MDICE), Kukruse low, Rakvere, Saunja, Moe, Hirnantian (HICE), Aeronian peaks, Rumba low, Valgu, and the Early Sheinwoodian (ESCIE) excursions. Additionally, a positive shift with an amplitude of *c*. 2‰ was identified in the lower part of the Nabala Regional Stage, middle Katian, in the Lelle core.

Preliminary results show that the trends in carbon isotope composition of bulk and palynomorph organic matter agree generally well with the $\delta^{13}C_{carb}$ curve. This is especially evident in the Llandovery and basal Wenlock, where the Rumba low and ESCIE display very similar amplitude and timing in both data sets. In the Middle and lower Upper Ordovician, the data are more scattered and the current sampling resolution does not provide an unambiguous solution. However, it seems that in this interval organic carbon is relatively heavier in relation to the $\delta^{13}C_{carb}$ curve than in the overlying strata. Change in the trend occurs near the base of the Katian, coinciding with biotic and facies turnover in the Baltoscandian basin and the globally traced Guttenberg carbon isotope excursion. Producing a higher resolution $\delta^{13}C_{org}$ curve from bulk organic matter is currently in progress and will allow for in-depth comparison with $\delta^{13}C_{carb}$ in the future.

Comparison between the carbon isotope composition of scolecodonts ($\delta^{13}C_{scol}$), chitinozoans ($\delta^{13}C_{chit}$) and bulk organic matter ($\delta^{13}C_{org}$) shows that scolecodonts are the lightest of the three in the Keila Regional Stage and younger strata. In the Darriwilian and Sandbian the bulk organic matter represents the isotopically lightest fraction. The relation between $\delta^{13}C_{chit}$ and $\delta^{13}C_{org}$ turned to be more variable in the current dataset. The largest offset between the three values was observed in the Darriwilian ($\delta^{13}C_{chit}$ - $\delta^{13}C_{org}$ = 2.8‰) and in the Nabala Regional Stage ($\delta^{13}C_{chit}$ - $\delta^{13}C_{scol}$ = 2.2‰). The difference between scolecodonts and chitinozoans was on average *c*. 1‰, and *c*. 0.5‰ if only the Silurian samples were taken into account. The latter value is very close to what has been observed previously on Gotland (Vandenbroucke *et al.* 2013).

Our results confirm that the isotopically light carbon in scolecodonts is typical not just of the Ireviken Event interval of one section, but represents a more general trait in the Katian through basal Wenlock in Baltoscandia. The low $\delta^{13}C_{scol}$ is incompatible with the generally assumed position of polychaetes in the trophic chain. However, some extant polychaetes are known to feed on microbial organic matter having their carbon isotopic composition lighter than that of the ambient fauna (Fisher *et al.* 2000). It is possible that in the early Palaeozoic, such feeding habit was more common, and a significant proportion of diet of the Late Ordovician and Silurian jaw-bearing polychaetes derived from microbial organic matter, perhaps including methanotrophs. Our data also suggest that an important change in the isotopic composition of organic matter occurred around the Sandbian–Katian boundary in the Baltoscandian basin. This may be due to changes in primary producer communities during the time period when Baltica reached subtropical latitudes and when the warm-water carbonate deposits first appeared in the region. However, it may also be that this is related to a more universal phenomenon and change in the global carbon cycling, ocean circulation and climate system. Data from other regions are necessary in order to examine this hypothesis further. Moreover, other proxy indicators such as lipid biomarkers and sulphur isotopes may provide additional hints to more fully understand the patterns reported herein.

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