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PAIRED ORGANIC AND CARBONATE CARBON ISOTOPE RECORDS THROUGH THE MIDDLE AND UPPER ORDOVICIAN OF ESTONIA

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Carbon isotopes have been in the standard toolbox for Earth history studies for several decades, helping to identify and interpret changes in carbon cycling, climate, environments and the biosphere. Carbon isotopic composition of Ordovician rocks has been documented from all major palaeocontinents, revealing a number of excursions with different magnitude and potentially different drivers. The largest of these is the Hirnantian Isotopic Carbon Excursion (HICE), which coincides with the end-Ordovician mass extinction. The Middle and Upper Ordovician succession of Baltoscandia has become a model area for studying carbon isotopes from bulk carbonates ($\delta^{13}C_{carb}$) and the Baltic standard curve (Ainsaar et al., 2010) serves as a basis for regional as well as intercontinental chemostratigraphic correlations. On the other hand, the carbon isotopic composition of organic matter ($\delta^{13}C_{org}$), is very poorly known from Baltoscandia and only few paired $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ records from restricted stratigraphic intervals are hitherto available from the Ordovician (e.g. Young et al., 2010). On a global scale, too, $\delta^{13}C_{org}$ data sets are rare and some intervals, like the Katian, are yet very poorly covered (Edwards & Saltzman, 2016). However, paired organic and carbonate carbon isotope data provide valuable constraints for identifying changes in biological fractionation and atmospheric pCO_2 and pO_2 (Edwards et al., 2017), and could also aid understanding the nature of both globally and regionally driven carbon isotope anomalies.

In this study we provide a new high-resolution paired $\delta^{13}C_{carb}$ – $\delta^{13}C_{org}$ data set from the Baltic Ordovician carbonate succession and examine if the $\delta^{13}C_{org}$ curve reveals the same features as the standard $\delta^{13}C_{carb}$ curve and explore if and how the offset between carbonate and organic matter trends varied in time. Another objective was to compare the new Baltic data with those recently published from other regions (e.g. Edwards & Saltzman, 2016) in order to assess the quality and chemostratigraphic potential of the new $\delta^{13}C_{org}$ records. We collected 211 samples for paired carbon isotope analysis from ca 200 m of Middle Ordovician to Llandovery strata of the Lelle (D-102) drill core, central Estonia. This section was selected for its representative palaeogeographic position on a carbonate platform setting within the Estonian shelf of the Baltic palaeobasin, as well as for its well-established biostratigraphy, sedimentology and geochemical context (e.g. Hints et al., 2007, Hints et al., 2017). The succession is represented mainly by limestones, which are partly dolomitic in the Darriwilian and Hirnantian, but otherwise of very low thermal maturity (CAI ~1).

The $\delta^{13}C_{carb}$ analyses were performed at the Department of Geology, Tallinn University of Technology, on a Thermo Finnigan Gasbench II coupled to a Delta V Advantage Isotope Ratio Mass Spectrometer. For $\delta^{13}C_{org}$ analysis, the insoluble residues were obtained by dissolving about 0.5 g of rock powder with 10 % HCl and were measured using elemental analyser Flash HT coupled with an isotopic ratio mass spectrometer Delta V Plus and Conflo IV at the Department of Geology, University of Tartu. Sample precision and calibration of data were performed using IAEA standards CH 3 and CH 6. TOC was less than 0.1 % in most samples, but exceeding 1 % in kukersite kerogen-rich basal Sandbian strata.

The bulk $\delta^{13}C_{carb}$ curve from the Lelle section exhibits variations between -1.5 and 4.5 ‰, revealing the main $\delta^{13}C_{carb}$ excursions known from elsewhere in the region: the Mid-Darriwilian excursion (MDICE), Kukruse low (LSNICE), Rakvere, Saunja, and Moe excursions and the prominent 4.5 ‰ HICE. Additionally, a positive excursion with an amplitude of c. 2 ‰ was identified in the lower part of the Nabala Regional Stage, middle Katian, and a brief negative excursion was observed in the Tõrremägi Member, basal Katian. The former was first reported from the Rapla section (Ainsaar et al., 2010) and the latter from several central Estonian sections (Bauert et al. 2017). Identification of the Guttenberg excursion (GICE) is only tentative, with bulk of this excursion missing due to a gap in the Lelle section.

The $\delta^{13}C_{org}$ values vary between ca -26 and -32.5 ‰. and the data are more scattered when compared to the $\delta^{13}C_{carb}$ curve, possibly due to variable sources of organic carbon. However, compared to data from other regions (e.g. Kozik et al. 2019, Li et al. 2018, Henderson et al. 2018), the Lelle $\delta^{13}C_{org}$ data set stands out by very little scatter and overall relatively low $\delta^{13}C_{org}$ values (long term average -30.3 ‰). In general, the $\delta^{13}C_{org}$ curve corresponds relatively well to the carbonate curve (Pearson correlation coefficient 0.65), and the above-mentioned $\delta^{13}C_{carb}$ excursions can all be recognized in the $\delta^{13}C_{org}$ data. MDICE and HICE are the most significant $\delta^{13}C_{org}$ events with slightly higher amplitude than the matching $\delta^{13}C_{carb}$ excursions. These can be used for global chemostratigraphy, but assessing the correlation of smaller excursions between continents needs additional high-resolution data. For purely chemostratigraphic purposes, the bulk carbonate curve remains nevertheless more robust tool.

The offset between carbonate and organic matter carbon isotope values ($\Delta^{13}C$, $=\delta^{13}C_{carb}-\delta^{13}C_{org}$) varies between 28.5 and 33.5 ‰. LOWESS smoothing of the Baltic data set revealed a time-constrained trend with $\Delta^{13}C$ values close to 30 ‰ through the Darriwilian and Sandbian, followed by ca 1.3 ‰ increase in baseline values near the expected position of GICE in the lowermost Katian. A decrease of similar amplitude occurs in the basal Silurian. Within this broad pattern some short-lived $\Delta^{13}C$ shifts may also be significant, for instance, in the upper Vormsi and lower Pirgu regional stages, where a rapid decrease and then increase in $\Delta^{13}C$ occurs; however, data from other sections are needed to confirm this. Young et al. (2010) documented a sharp 3 ‰ $\Delta^{13}C$ peak in the Hirnantian of the Kardla core, southern Estonia, but this feature was not revealed in the Lelle data set, where Hirnantian $\Delta^{13}C$ values are very similar to those in the Katian.

Based on data compilation mostly from Laurentia, Edwards & Saltzman (2016) documented a gradual long-term increase in $\Delta^{13}C$ values through the Lower and Middle Ordovician, which they attributed to changes in biological fractionation and increasing pO_2 levels. The new $\Delta^{13}C$ trend from the Lelle core also shows an increase, but in details the pattern is different – a major change in fractionation appears to be more abrupt and occurring later than suggested by Edwards & Saltzman (2016). It is possible that the Lelle $\Delta^{13}C$ trend carries a stronger imprint of regional or local drivers. First, during the same time interval the drift of Baltica towards tropical latitudes caused changes in climate and facies patterns in the Baltic palaeobasin and linked shifts in ecosystems, including the primary producer communities. This might have had impact on carbon isotopic fractionation through multiple scenarios. Second, even though the $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ signatures appear to be well-preserved in the Lelle core, the effects of local depositional settings and minor diagenetic overprints should not be overlooked as shown by Richardson et al. (2019) working on an early Silurian succession from Estonia. An alternative explanation of the Lelle $\Delta^{13}C$ trend is that it reflects a more universal pattern associated with perturbation in the global carbon cycling, ocean-atmosphere system and climate that is marked by the early Katian Guttenberg $\delta^{13}C$ excursion and the following volatile interval of carbon isotope composition (Kaljo et al., 2007). At the same stratigraphic level several fossil groups show the beginning of a longer diversity decline that Kaljo et al. (2011) called the Katian prelude to the Hirnantian mass extinction.

In summary, the new paired carbonate and organic matter carbon isotope records from the Lelle core are the first stratigraphically long high-resolution data from Baltica and allow filling gaps also in the global data compilation. The revealed trends may be significant and suggest time-constrained changes in carbon fractionation close to GICE interval, but additional Baltic sections need to be studied in order to explore the spatial variability of $\delta^{13}C_{org}$ and $\Delta^{13}C$ trends across the basin.

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