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Palaeozoic carbon isotope excursions and carbonate component analysis

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Palaeozoic carbonate $\delta^{13}C$ studies have mainly focused on bulk rock analysis in chemostratigraphic correlations and palaeoenvironmental interpretations, assuming limited isotopic heterogeneity of samples. Particular attention has been paid to positive $\delta^{13}C$ excursions, which likely reflect climatic events. However, several studies have provided isotope data from different rock components demonstrating significant sample-scale variation of $\delta^{13}C$ values.

We describe the isotopic and elemental composition of individual components in carbonate rocks and analyse which components carry the primary depositional isotopic signatures and which components have been isotopically reset by diagenetic processes. The comparison of bulk rock and component-specific data allows us to assess the reliability of isotopic data used in environmental reconstructions and offers an opportunity to better reconstruct magnitudes of $\delta^{13}C$ excursions and related dynamics of seawater dissolved inorganic carbon.

Here we focus on the Hirnantian Isotopic Carbon Excursion (HICE) at the end of the Ordovician period and the Mid-Ludfordian Carbon Isotope Excursion (MLCIE) during the late Silurian period. Previous bulk rock studies have demonstrated the occurrence of the HICE in multiple Estonian drill cores corresponding to the Porkuni Regional Stage. The HICE samples from the Kamariku, Karinu, and Otepää drill cores were subsampled by micro-drilling, and isotope analysis of individual components was done by isotope-ratio mass spectroscopy (IRMS). Limited sample-scale heterogeneity and good correspondence with bulk rock $\delta^{13}C$ values are seen in micritic carbonate samples, whereas different bioclastic and cement components in wackestone and grainstone samples exhibit up to 4‰ range of $\delta^{13}C$ values with some components having $\delta^{13}C$ values up to 3‰ higher than the bulk rock values. Lithologically heterogeneous grainstone from the Otepää core shows $\delta^{18}O$ variability as much as 3‰ and ooids carrying the lowest, most overprinted values.

Isotope results obtained by the Secondary Ion Mass Spectrometry (SIMS) on MLCIE samples from Lithuanian Vidukle drill core show up to 5‰ range of $\delta^{13}C$ values, and some values are up to 4‰ higher than the bulk rock values. A similar range can also be seen in $\delta^{18}O$ values. Our results demonstrate that multi-component wackestone and grainstone samples from HICE and MLCIE intervals are isotopically heterogeneous and that heterogeneity needs to be accounted for in reconstructions of the past carbon cycle and $\delta^{13}C$ curves.

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