

Phase- and facies-specific carbon, clumped, and calcium isotopes of the Kinderhookian-Osagean Boundary Excursion

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The Kinderhookian-Osagean Boundary Excursion (KOB) is one of the largest positive carbon isotope excursions in the Phanerozoic. Possible end-member interpretations of these and other Paleozoic positive carbon isotope excursions include burial diagenesis, meteoric diagenesis associated with global sea level fall, phase-specific isotope effects, local to platform-scale variations in the $d^{13}\text{C}$ of DIC, or increased carbon burial. Exceptionally preserved carbonates from the Early Mississippian Gilmore City Formation in north-central Iowa provide an opportunity to integrate facies analyses, petrography, and geochemistry of the excursion interval.

The top several meters of both cores exhibit depleted $d^{13}\text{C}$, fluid $d^{18}\text{O}$, and $d^{44/40}\text{Ca}$ compositions, elevated manganese concentrations, and vertical calcite-filled fractures, all consistent with meteoric diagenesis. Below this, however, mineral $d^{18}\text{O}$ does not increase alongside changes in D_{47} , evincing sediment-buffered diagenesis in lower portions of the core. Low clumped isotope (D_{47}) temperatures (median = 32°C), seawater-like fluid $d^{18}\text{O}$ values (median = -1.3‰), and preservation of original carbonate fabrics at the petrographic scale all suggest that carbonates faithfully record the onset and main phase of the KOB. TD_{47} and $d^{18}\text{O}$ data from sediment-buffered intervals show $3\text{--}5^\circ\text{C}$ cooling associated with the positive $d^{13}\text{C}$ excursion of $\sim 3\text{‰}$ in these sections.

We do not observe a strong dependence of $d^{13}\text{C}$ composition on facies in our measured sections. The peloidal to fossiliferous grainstone facies that carries the peak of the KOB is also present above and below the excursion; algal cortoids are present at the peak of the excursion ($\sim 6\text{‰}$) as well as on the falling limb ($\sim 3\text{‰}$). Trends in $d^{13}\text{C}$ persist across parasequence boundaries with only minor shifts, indicating a subordinate role for facies changes in the overall excursion.

Phase-specific isotope analyses of crinoid ossicles, most abundant during the excursion peak, show a median $+0.8\text{‰}$ $d^{13}\text{C}$ offset (maximum $+1.7\text{‰}$) from coeval bulk carbonate. Point-counting of thin sections shows that crinoids comprise no more than 60% of fossiliferous grainstones; thus, we estimate the maximum effect of elevated crinoid $d^{13}\text{C}$ to be $\sim 0.5\text{‰}$. Preliminary measurements of crinoids, rugose corals, and brachiopods tend to have cooler D_{47} temperatures and limited to