

# 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 =  $32^\circ\text{C}$ ), seawater-like fluid  $d^{18}\text{O}$  values (median =  $-1.3\text{‰}$ ), and preservation of original carbonate fabrics at the petrographic scale all suggest that carbonates faithfully record the onset and main phase of the KOB.  $\text{TD}_{47}$  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