



Mikko Kriek

Carbon cycle perturbations at the Frasnian-Famennian boundary in the Illinois Basin, USA

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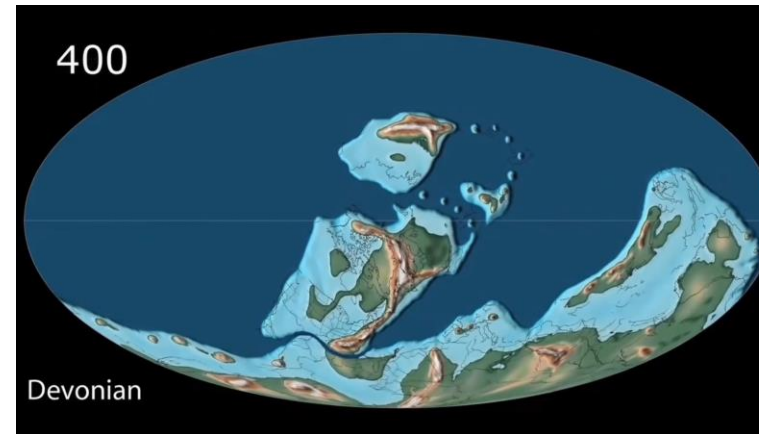
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Devonian Paleogeography

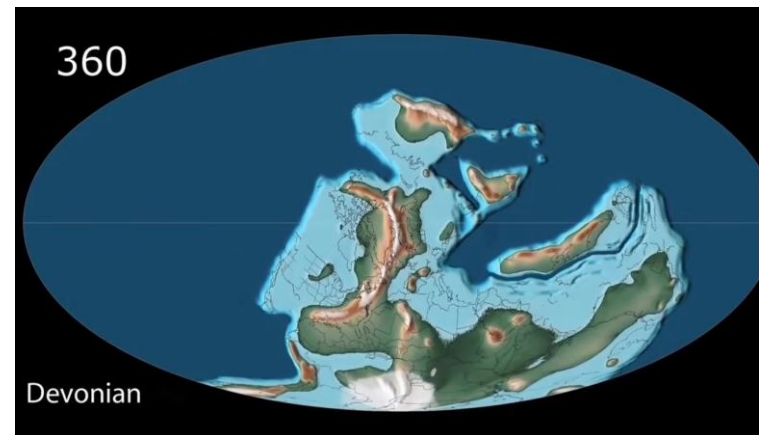
North America - Mostly epeiric seas

- ~420 – 405 Ma:
 - Collision of Laurentia, Avalonia, and Baltica → Acadian and Caledonian orogenies
 - Resulting landmass: Euramerica (Laurasia)
- Devonian marks evolution of:
 - Terrestrial arthropods
 - Terrestrial vertebrates
 - Terrestrial plants
 - Diversification of jawed fishes
- Coral reefs thrived up until Late Devonian extinction (severely affected)

Early Devonian

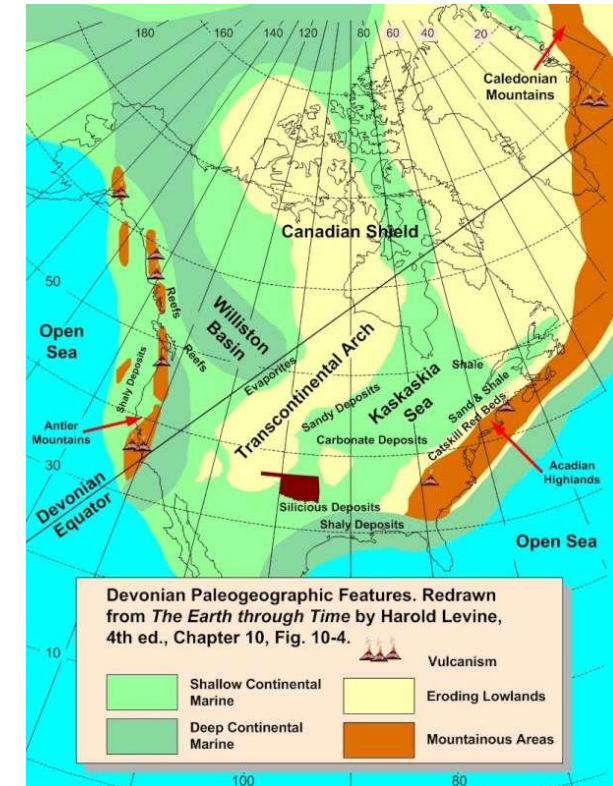


Late Devonian



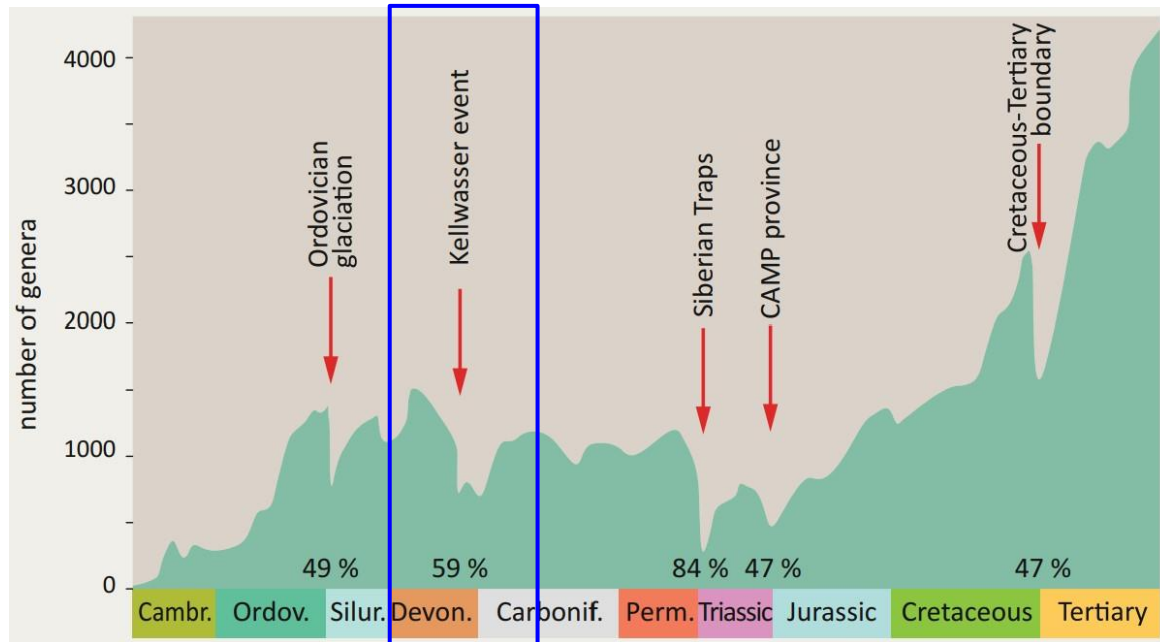
*Number marks Ma

(Scotese, 2016)



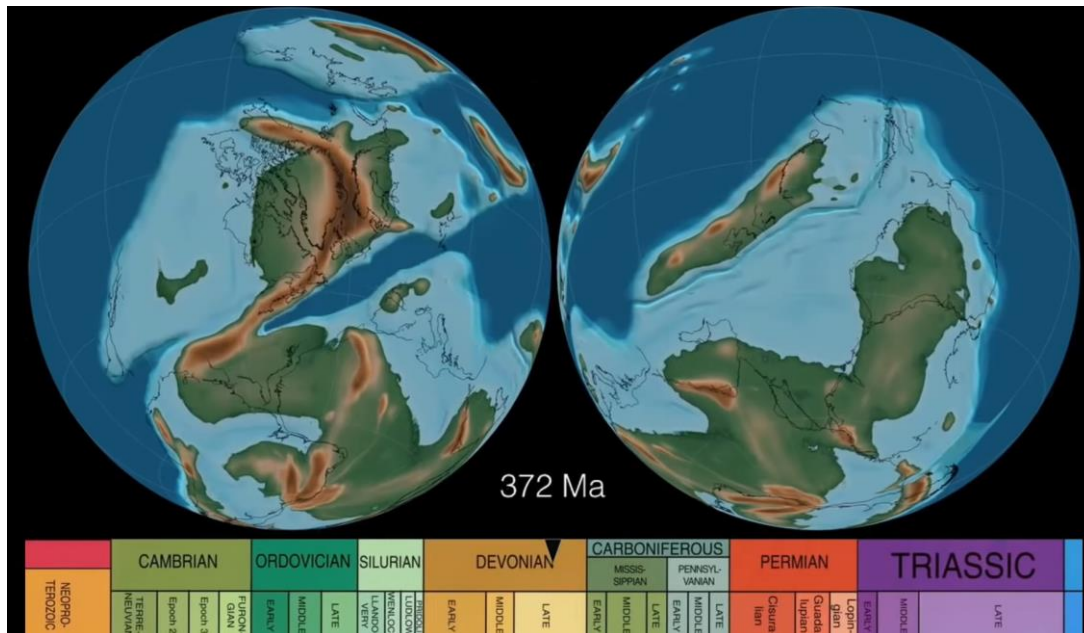
Based on (Koenig, 1967)

Late Devonian Extinction



(Meschede and Warr, 2019)

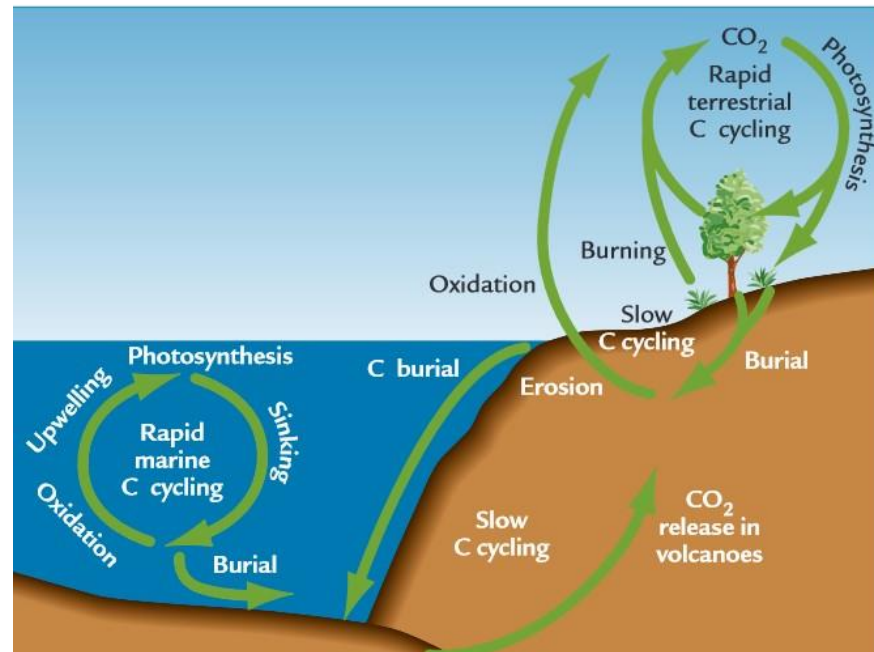
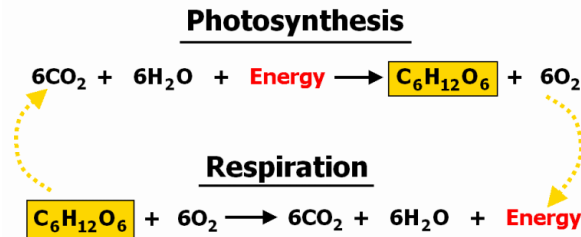
- Late Devonian extinction (~70-82% extinct) – unique timing of biodiversity loss
- 2 major events: Kellwasser Event (KWE) and Hangenberg Event
 - KWE has two parts:
 - 1st: Lower Kellwasser Event (LKE)
 - 2nd: Upper Kellwasser Event (UKE) at F-F Boundary
- Many suggestions: Volcanism, weathering, glaciation, asteroid impacts
- Speciation decline also discussed
- Marine invertebrates severely impacted.
- Many major hypotheses relate to **marine anoxia**.



(Scotese, 2019)

Geochemical Cycling, ^{13}C : ^{12}C , & Marine Anoxia

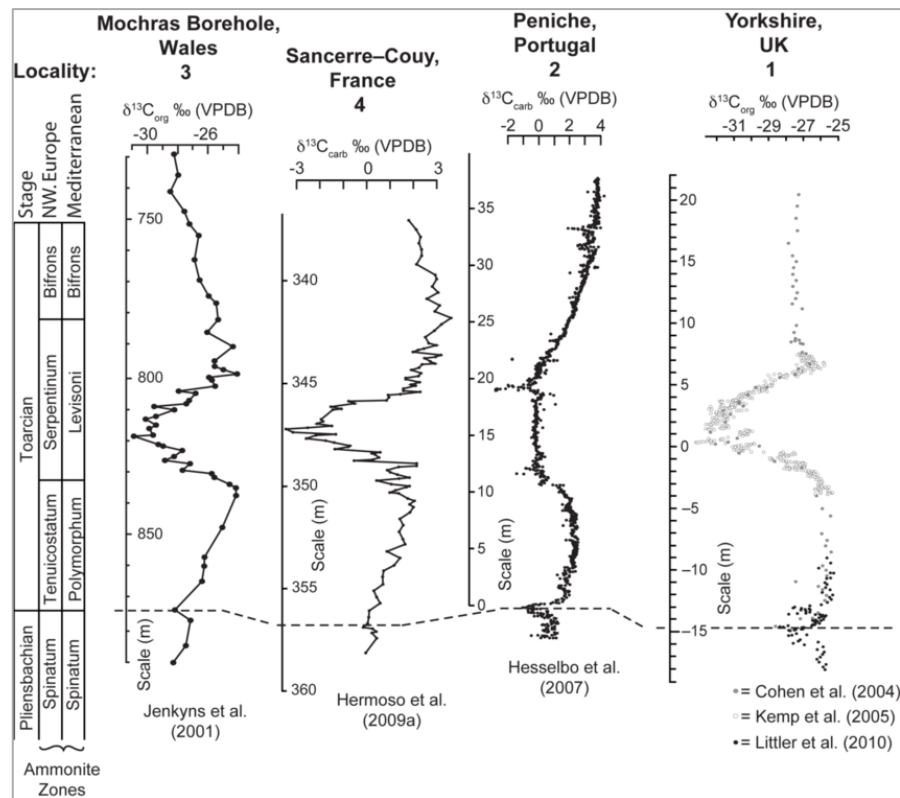
- ^{12}C and ^{13}C : stable isotopes, used to learn about biogeochemical conditions at time of deposition
- C isotope excursions influenced by varying:
 - Marine primary productivity
 - Marine microbial respiration
 - Organic carbon burial
 - Input of exogenic carbon (volcanic, methane clathrates)



(Ruddiman, 2014)

- Greater $\delta^{13}\text{C}$ values in the oceans can mean increased primary productivity
 - Phytoplankton prefer ^{12}C over ^{13}C
- Marine anoxia: no $\text{O}_2 \rightarrow$ organic matter (OM) buried not fully decomposed
 - OM burial removes isotopically light carbon
 - This leaves the oceans enriched in heavier carbon isotopes
 - These heavier carbon isotopes can be preserved in marine sediments (carbonate and organic matter)

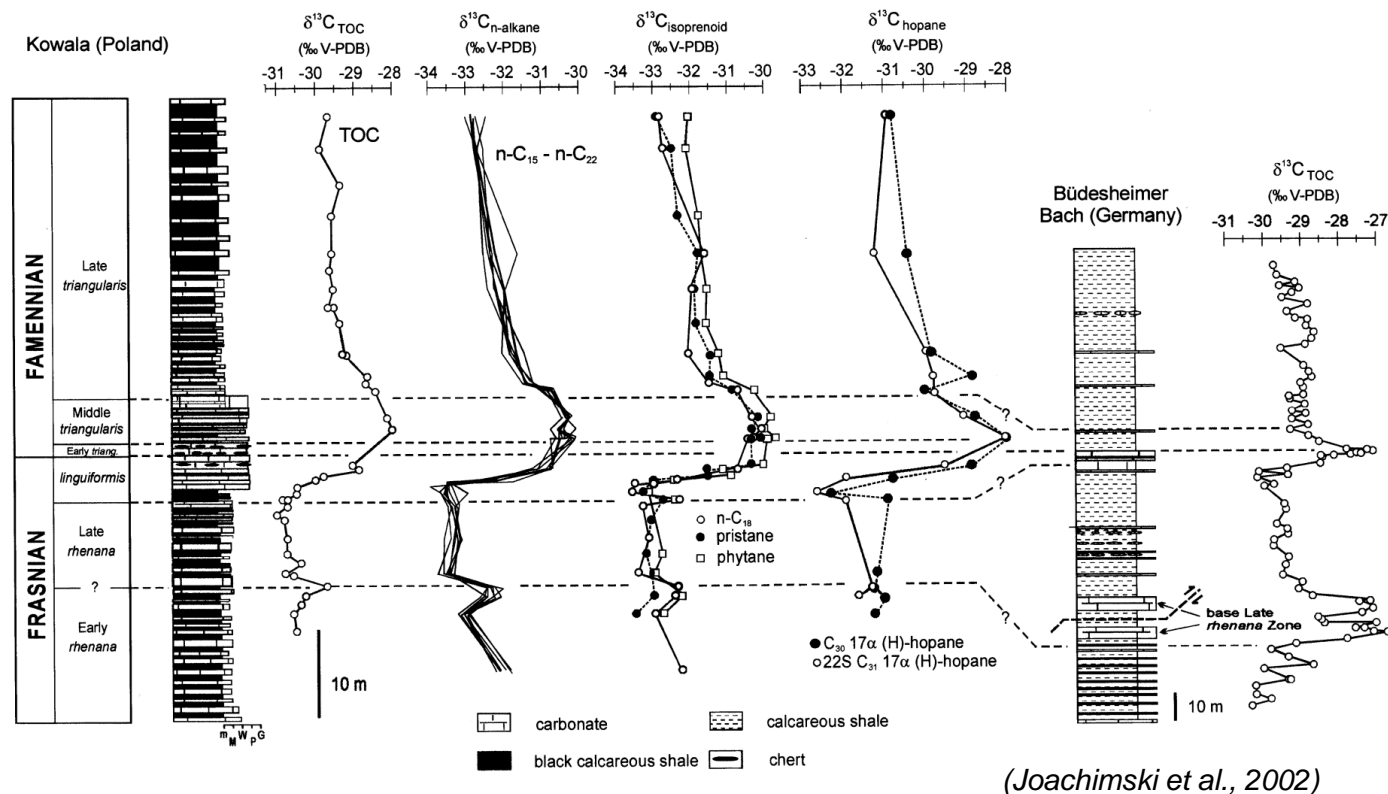
$\delta^{13}\text{C}$



Negative CIE in early Toarcian

(Caruthers, 2013)

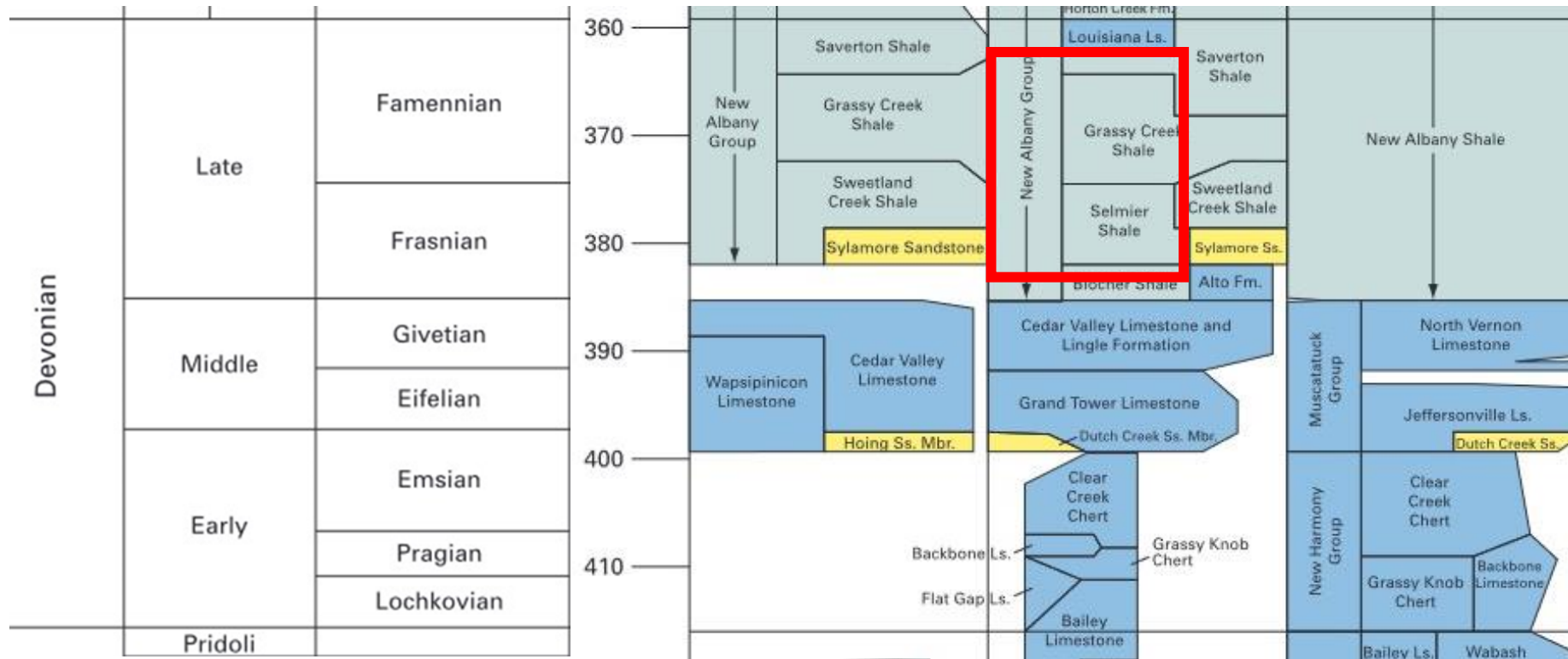
- Mass extinctions commonly associated with isotope excursions
- Multiple mass extinctions with negative $\delta^{13}\text{C}$ excursions, such as the End-Permian (P-Tr) and the Toarcian
- Some others related to positive $\delta^{13}\text{C}$ excursions, such as the Late Devonian



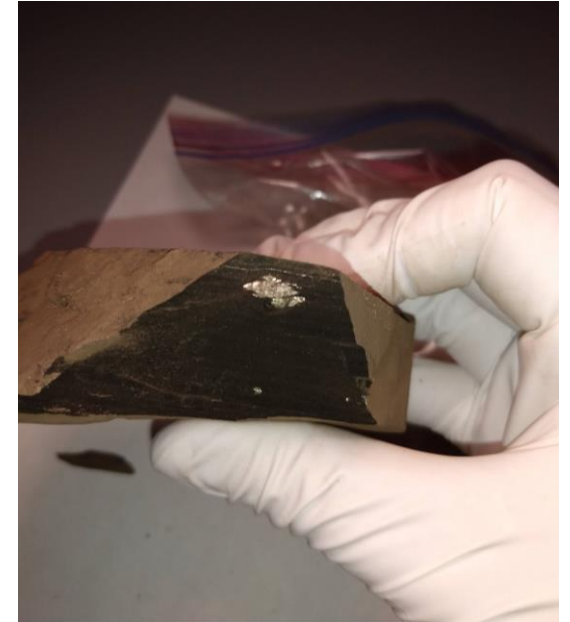
Carbon Isotopes & the Kellwasser Event

- Both UKE and LKE marked by changes in $\delta^{13}\text{C}$
 - $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{\text{carb}}$ respond with similar magnitude excursions
- Around F-F boundary/UKE, significant $\delta^{13}\text{C}$ positive excursion (~2 ‰)
- This was likely driven by marine anoxia associated with the KWE

Illinois Basin stratigraphy



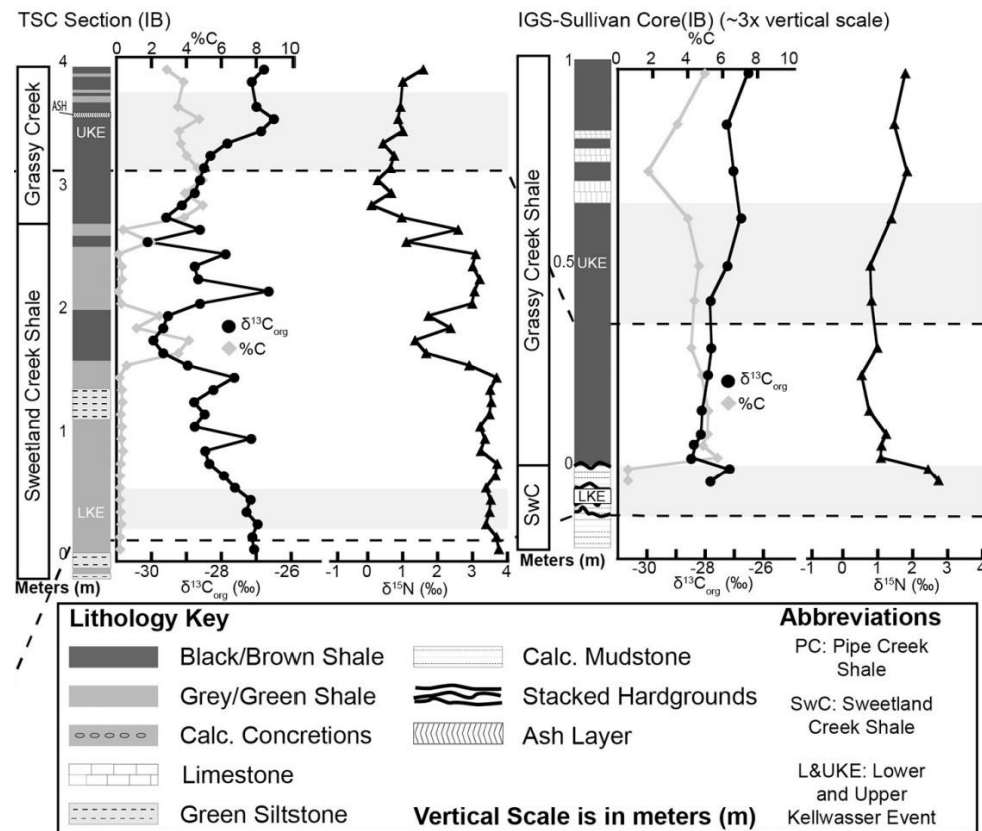
(Swezey, 2009 from USGS)



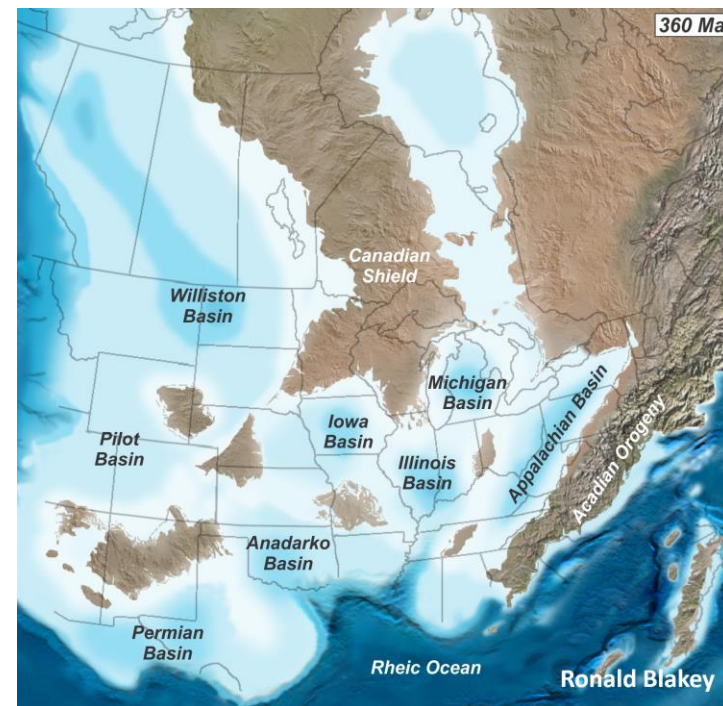
- Illinois Basin → an epeiric sea in Euramerica during Devonian
- Our samples cover Selmier and Grassy Creek Shales; primarily black shales
- **Selmier and Grassy Creek members**
 - Part of New Albany Group: mid-Devonian to early Mississippian
 - Selmier – green/gray shale
 - Grassy Creek – black shale

Illinois Basin: Previous work

- Illinois Basin: 2 depocenters
 - Southeast and Northwest
 - Possibly separated by a shallow sill
- Uveges et al. (2019) measured $\delta^{13}\text{C}_{\text{TOC}}$ & $\delta^{15}\text{N}_{\text{Bulk}}$ in Illinois and Appalachian Basins
 - Results: + $\delta^{13}\text{C}_{\text{TOC}}$ excursions, expected from KWEs.
 - This study was from the Northwest depocenter



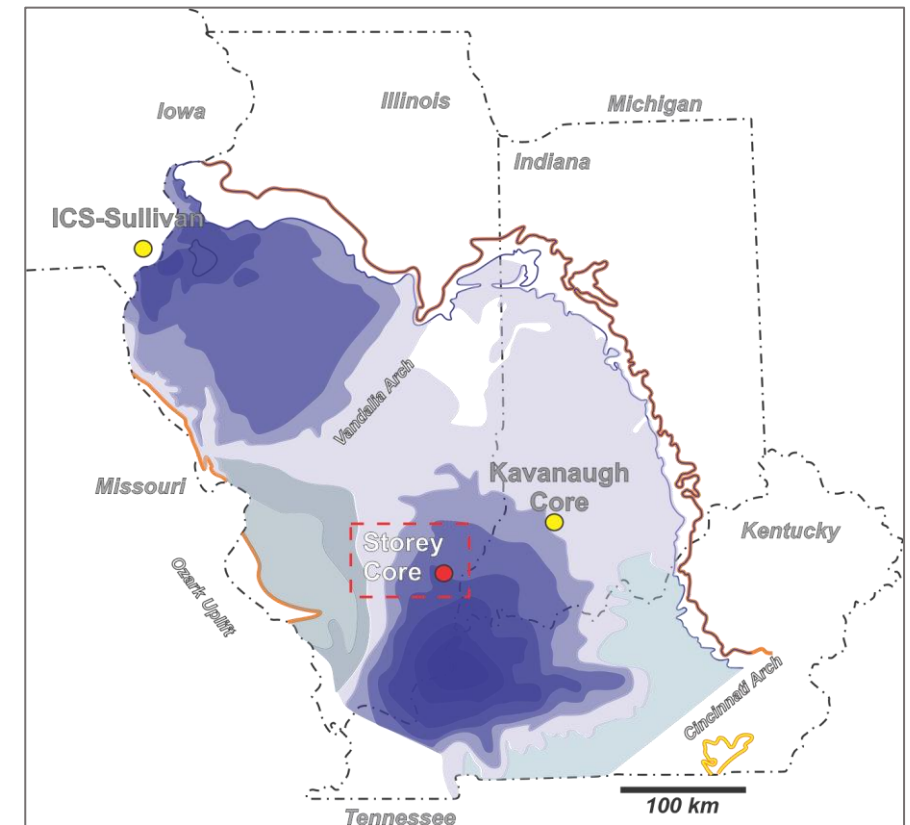
(Uveges et al., 2019)



In the mid-late Devonian, North America covered largely by epeiric seas – including the Illinois Basin (IB)

Study Location

- $\delta^{13}\text{C}$ enrichment identified in North America, but more focus on carbonate than TOC.
- Study focus: Is there a change in $\delta^{13}\text{C}$ in the Southeast Illinois Basin, and will it indicate preservation of UKE?
- Samples are from the Storey Core (Southeastern Illinois)
- New Albany Group: Selmier + Grassy Creek



Methods

- Storey Core: Measuring $\delta^{13}\text{C}_{\text{TOC}}$ from 30 samples
 - Depths 1518 – 1580 m

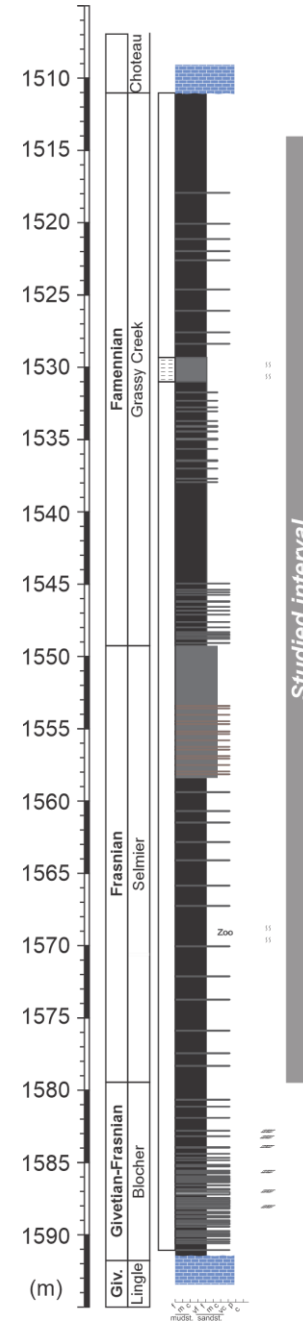
1. Sample preparation: Samples powdered with ball mill, + multiple rounds acidification

2. Mass Spectrometry: Organic $\delta^{13}\text{C}$ isotopes measured at UCSC's Stable Isotope Laboratory, with help from U-Maryland

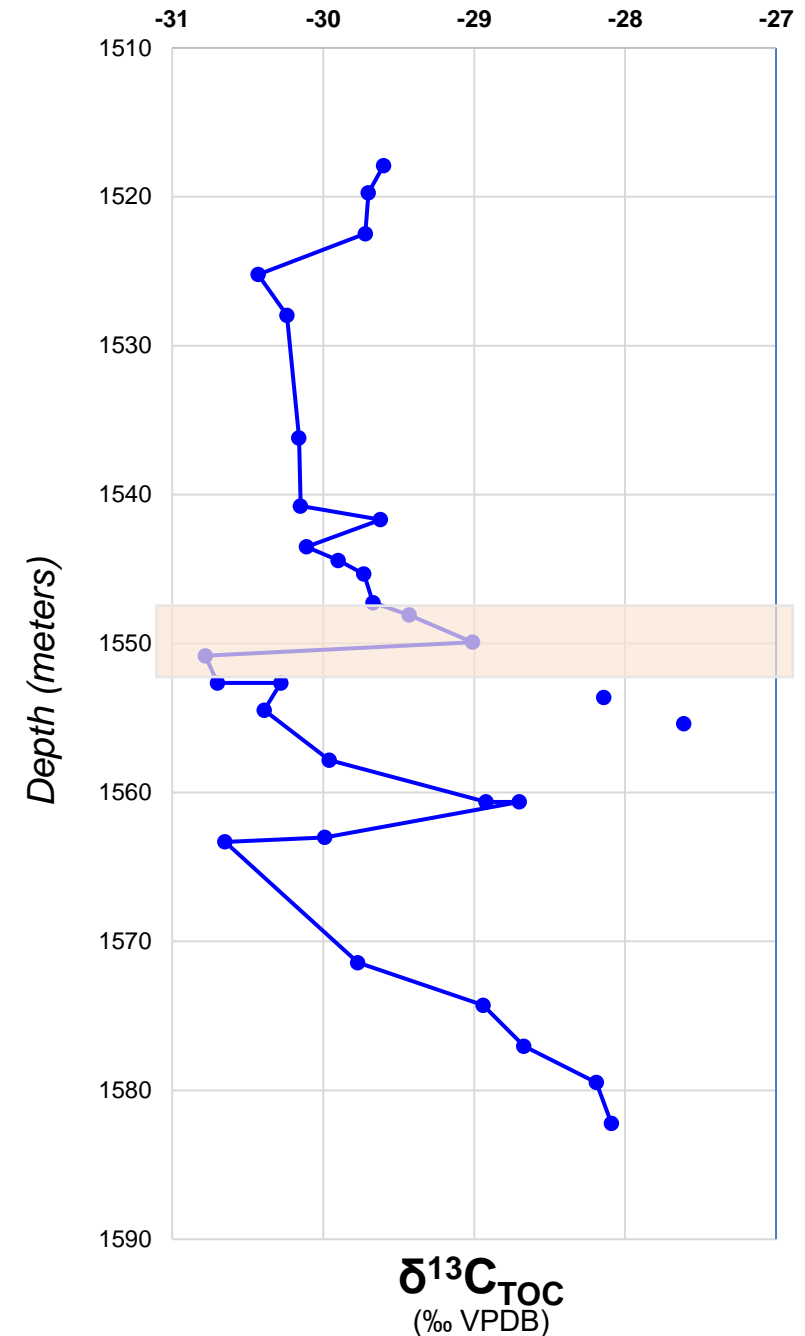
- Additional data from 96 samples (Mo, U, Zr) measured with X-ray fluorescence at University of Texas, Permian Basin

Results

- +2‰ excursion in $\delta^{13}\text{C}_{\text{TOC}}$ at ~1550.8 – 1549.9 meters, at what may be Frasnian-Famennian Boundary
 - -31‰ to -29‰
- Other variability ~1560m?
- Future research question → What is expression of Lower Kellwasser?
- Outliers ~1555 meters

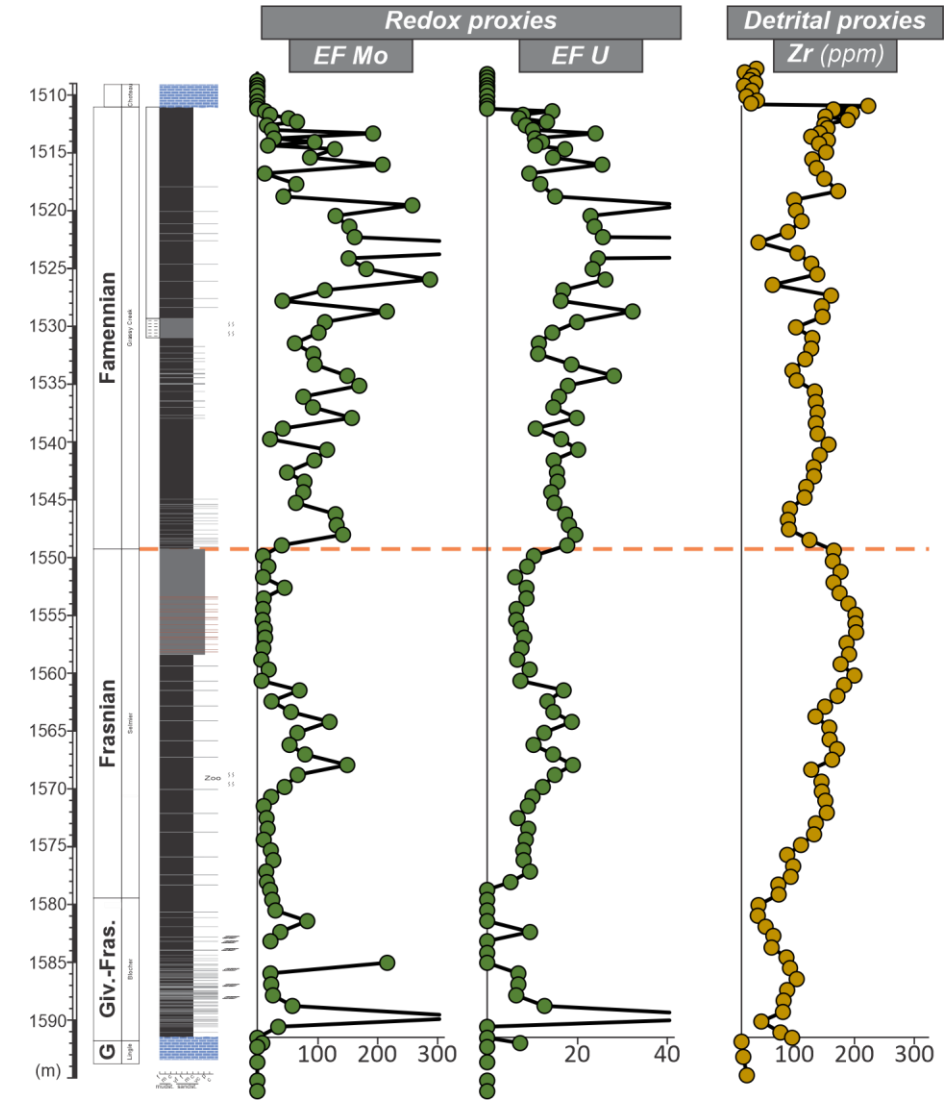


Storey Core - New Albany Shale



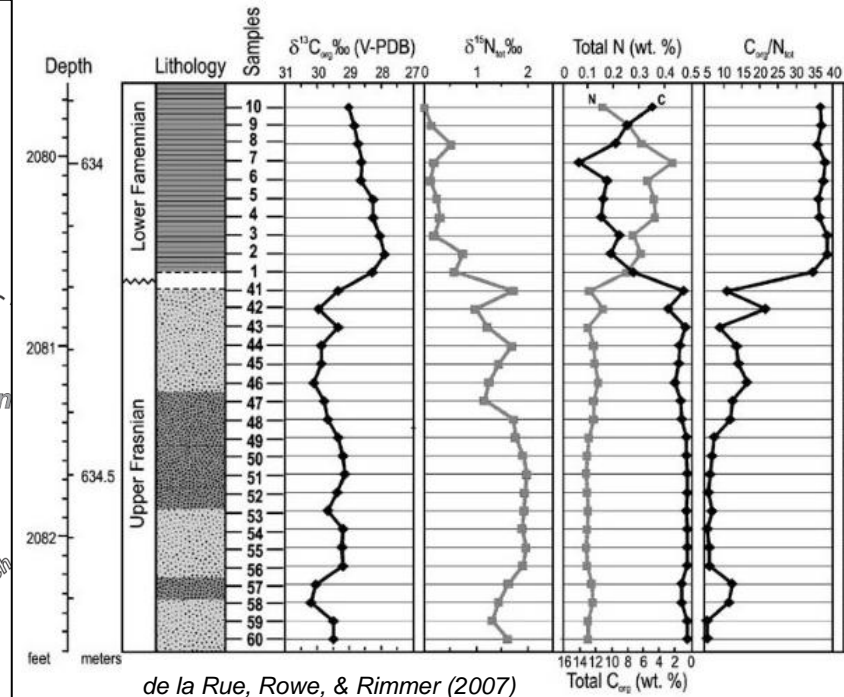
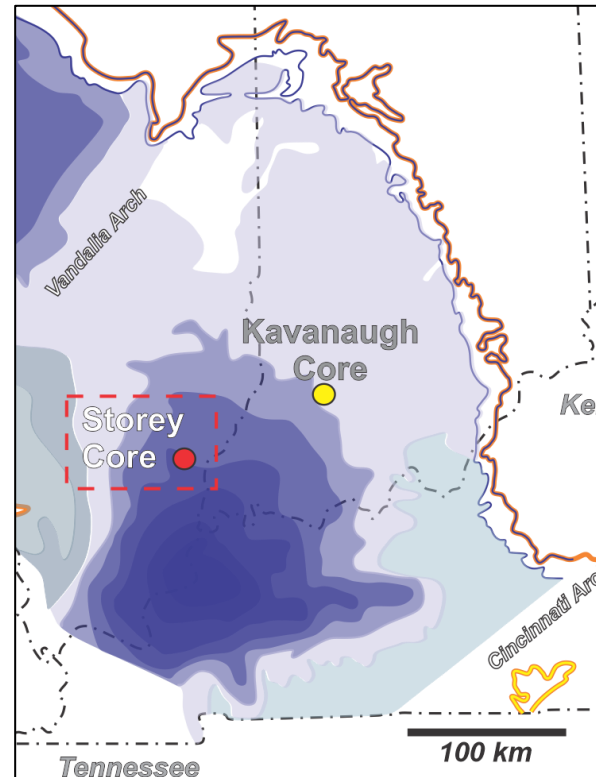
Supporting Data: Trace Elements

- Increased Mo and U values in Storey Core
 - Mo and U concentrations used to assess redox changes
 - Increasing Mo and U coincident with positive $\delta^{13}\text{C}$ excursion indicates expanding anoxia
- Decrease in Zr values
 - Used to assess changes in detrital input
 - Can indicate sea level changes
 - Decreasing Zr coincident with positive $\delta^{13}\text{C}$ excursion indicates marine transgression

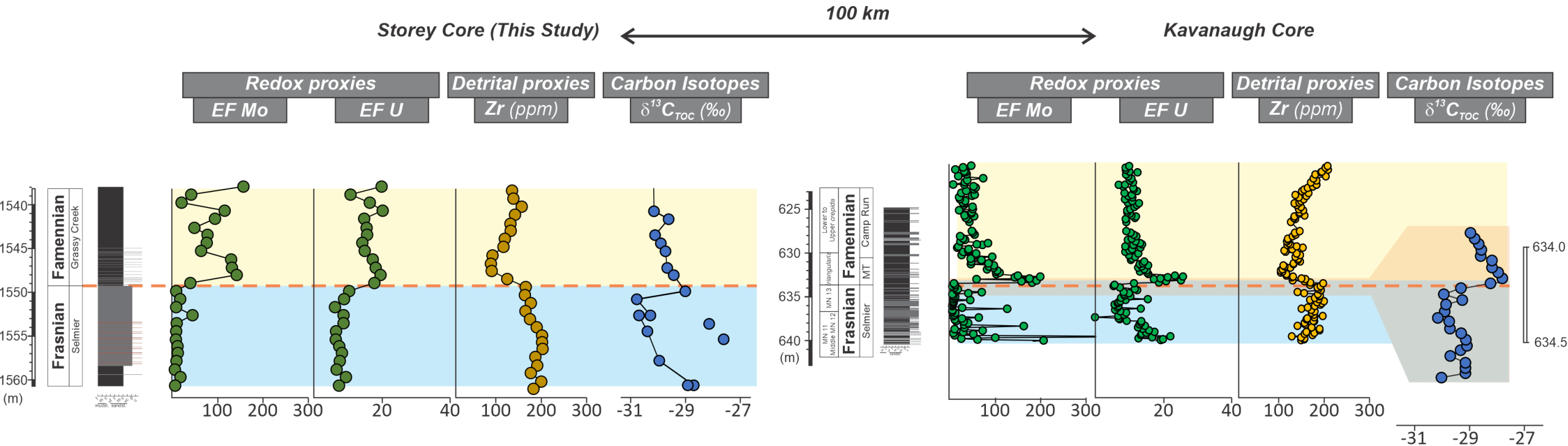


Supporting Data: Kavanaugh Core

- Previous studies in SE depocenter of the Illinois Basin
- *De la Rue, Rowe, & Rimmer (2007)*: measured $\delta^{13}\text{C}_{\text{TOC}}$ in the Kavanaugh Core, ~100 km NE of the Storey Core in shallower part of basin.
- Findings: +2‰ $\delta^{13}\text{C}$ excursion, likely preservation of UAE



Comparison to Kavanaugh Core



- Evidence from the 2007 study (*de la Rue et al.*) showed 2‰ increase in $\delta^{13}\text{C}_{\text{TOC}}$ for Kavanaugh Core
- Same trend in Mo, U, Zr, & carbon isotopes seen in both cores
- Carbon isotope excursion associated with expanded anoxia and marine transgression at Frasnian-Famennian boundary

Conclusion

- **Comparison of $\delta^{13}\text{C}_{\text{TOC}}$ values in Kavanaugh & Storey Core shows high likelihood of UKE preservation in southeast IB**
 - Based on +2‰ excursion of $\delta^{13}\text{C}_{\text{TOC}}$ values in Storey Core from New Albany Shale
 - Related to possible expansion of anoxic conditions in the Illinois Basin
 - Related to marine transgression

Acknowledgements

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- ...For their generous support of this project through funding and resources.
- Thank you for listening!