Evaluating Ocean Oxygenation: A Redox Study of Middle Ordovician Carbonates

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Introduction

The Paleozoic Era contains two significant biological radiations, although the cause of these 'explosions' remains elusive. The Great Ordovician Biodiversification Event (GOBE) occurred some 40 million years after the Cambrian Explosion of animals, replacing the earlier faunas with a wide variety of suspension feeders and pelagic animals. Middle Ordovician carbonates near Strasburg, Virginia, preserve the steep onset of the GOBE and consist of organic-rich limestones and shales from supratidal to deep subtidal and continental slope depositional environments. This study aims to use carbonate redox proxies to explore changes in marine oxidation states as a possible cause of the GOBE.

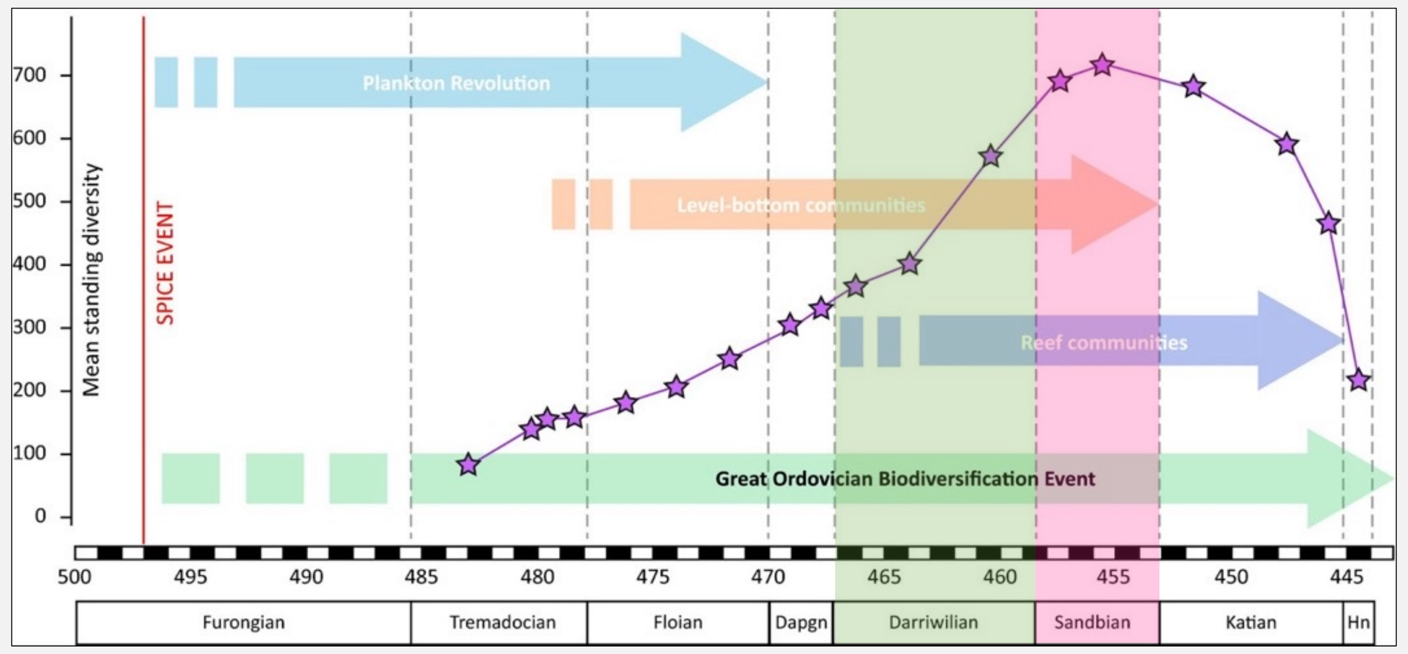


Figure 1. An illustration of the GOBE with a focus on the reef, plankton, and benthic communities. The SPICE event is a notable positive carbon isotope excursion in the late Cambrian Period. The purple stars represent data compiled by Kröger & Lintulaakso (2017) and presented by Servais & Harper (2018).

Hypothesis

Null hypothesis: Redox states in carbonate proxies show **no change** in marine oxygen levels in the Middle Ordovician relative to times before and after the event.

Working hypotheses: Marine oxygen levels **increased or decreased** in the Middle Ordovician oceans as indicated by redox states in carbonate proxies.

Methods

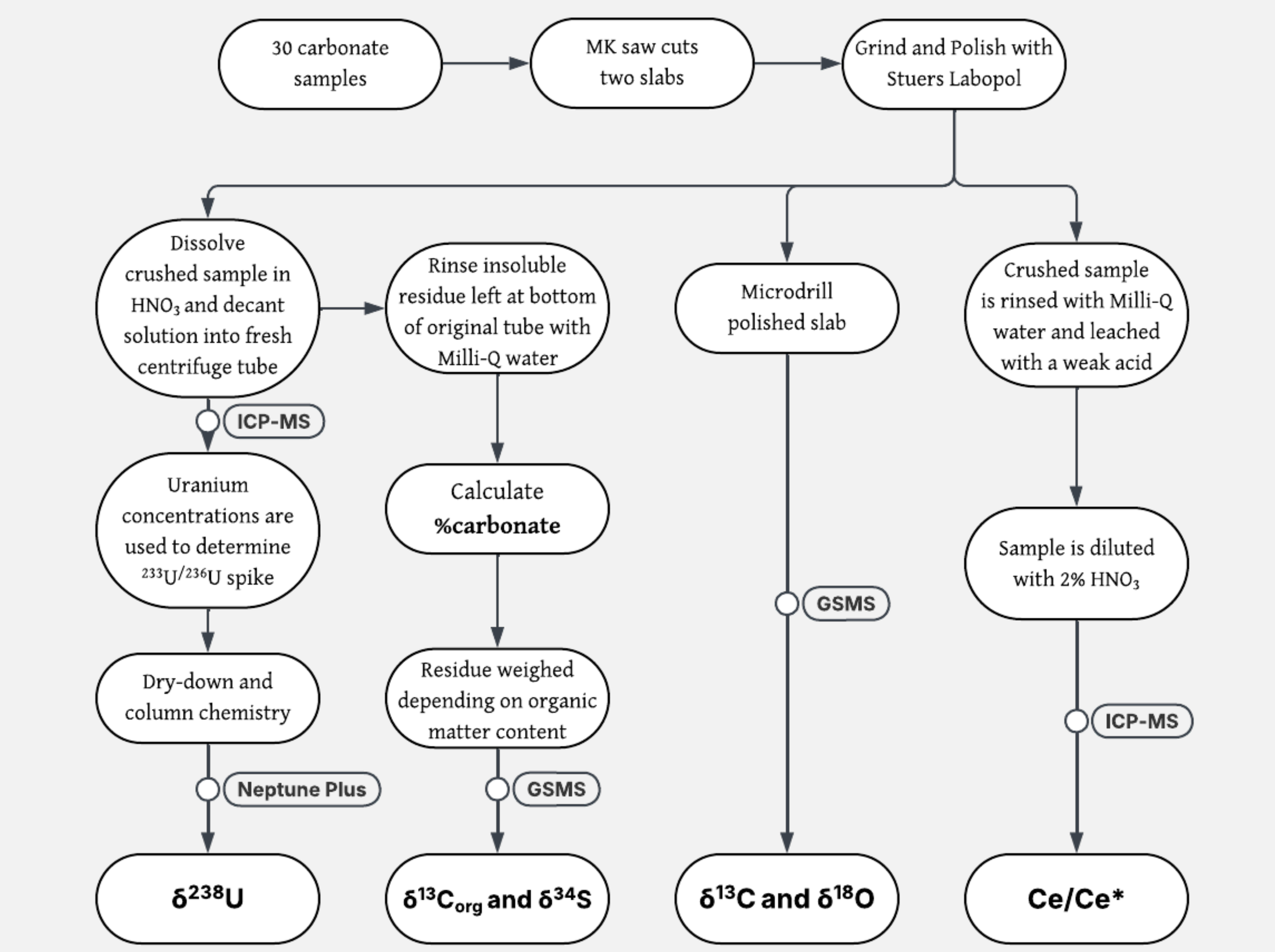


Figure 2. Flowchart of methods for analysis of Ordovician carbonate samples.

Results

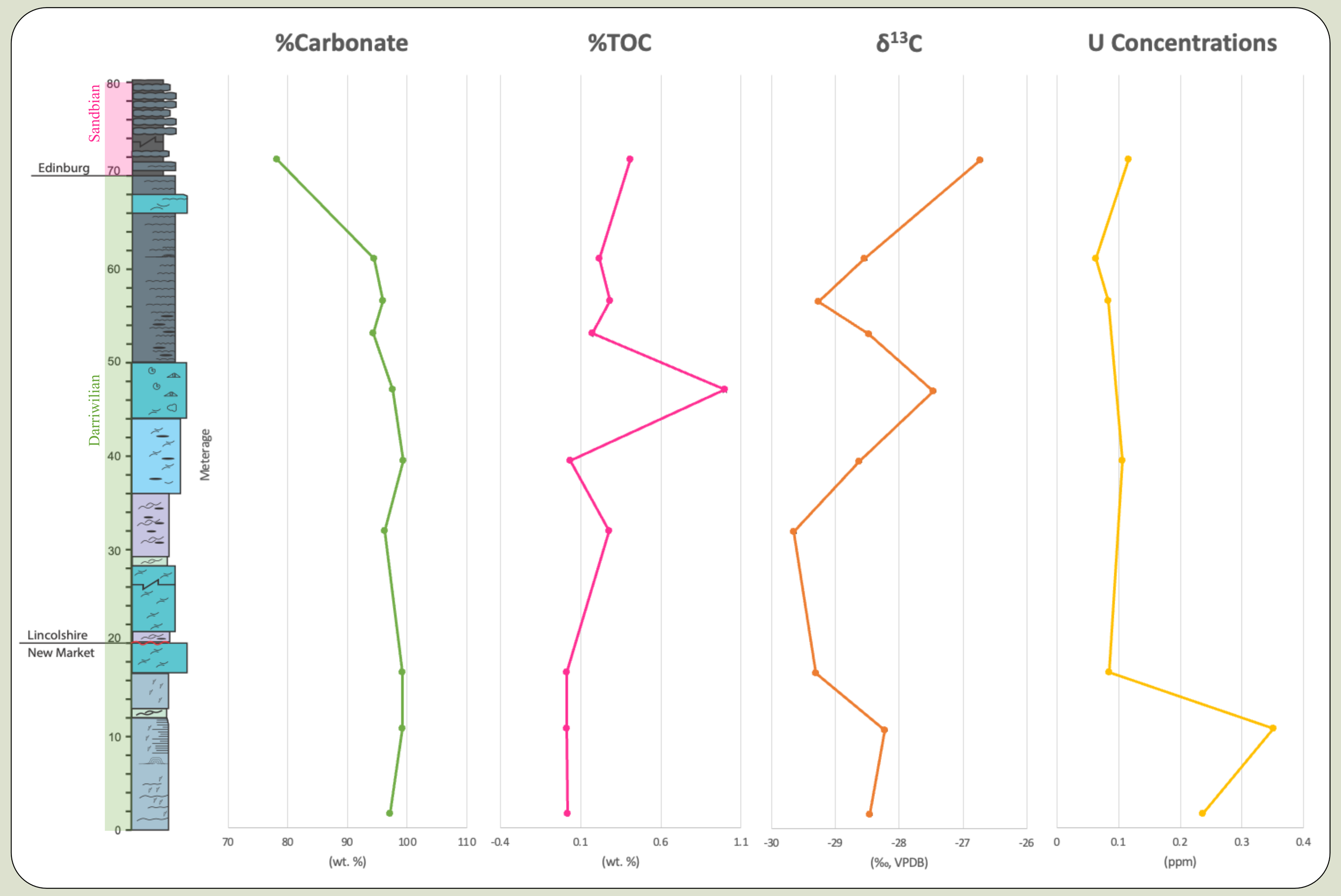


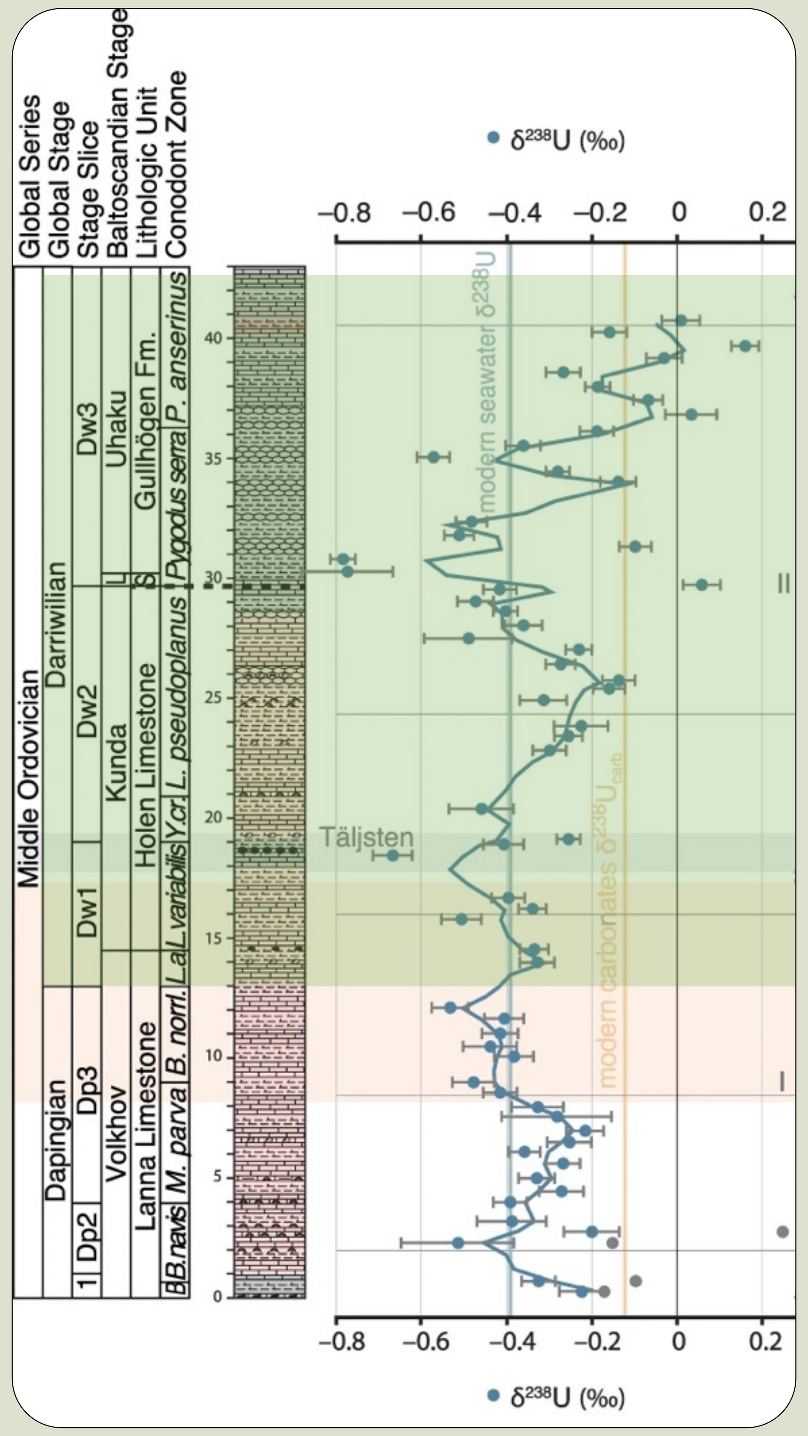
Figure 3. Chemostratigraphic plot showing the correlations between $\delta^{13}C$, %TOC, %carbonate, uranium concentrations and stratigraphic height. The carbonate content in ten carbonate samples ranged from 78.13% to 99.75%, with an average of 95.56±6.09% (1σ). Total organic carbon values in ten carbonate samples ranged from 0.013% to 0.998%, with an average of 0.22±0.29% (1σ). Carbon isotope values from ten organic carbon residue samples ranged from -26.73% to -29.31%, with an average of -28.48±0.87% (1σ). Uranium concentrations in seven carbonate samples ranged from 0.063 ppm to 0.351 ppm, with an average of 0.149±0.106 (1σ).

Figure 4,5,6. Figure 4 (top left) shows a view of the contact between the Beekmantown dolomite and the New Market limestone representing the Knox unconformity (highlighted by a red line). Figure 5 (top right) shows a roadside view of the New Market and Lincolnshire. The formations are separated by an unconformity, highlighted by a red line. Figure 6 (bottom left) shows a view of the alternating shale and nodular carbonate beds that make up the Edinburg Formation. Overall, the successions displayed features consistent with deepening waters and increasing erosion, potentially driven by tectonic activity. All these photos were taken at Battlefield Road in spring 2025 when 19 additional samples were collected to provide better insight.

	Average	Std. Dev	Offset
13C urea	-34.07	0.03	4.68
%C urea	20.00	1.32	1.00
Intensity RSD	3.77	4.43	

Figure 9. The uncertainties for uranium concentrations are reported as relative standard deviation (RSD) and was determined to be 3.77% for this analytical session, which is a favorable result. If the RSD is high, it typically means that the ICP-MS instrument had trouble distinguishing the sample from the background noise and thus could not get a clean measurement. The average $\delta^{13}C$ composition for 13 urea samples run during the analytical session on the GSMS was -34.07‰ (true value is -29.39‰) with a standard deviation of 0.03‰ and the abundance was 20.00 wt% (true value is 20 wt%) with a standard deviation of 1.32 wt%.

Figure 7. A plot of $\delta^{238}U$, from the only known study of uranium isotopes associated with the GOBE, revealed more negative $\delta^{238}U$ compositions in carbonates from Sweden in the interval before and at the onset of the GOBE (displayed with a yellow highlight). Uranium isotope values are more negative, indicating widespread anoxia before an increase in $\delta^{238}U$ and oxic conditions. (Rey et al., 2022). This may thus explain the unusually low uranium concentrations in my sample suite due to the depletion of uranium in anoxic environments. My study will capture the peak of the GOBE which is not reflected in this study.



Systematics

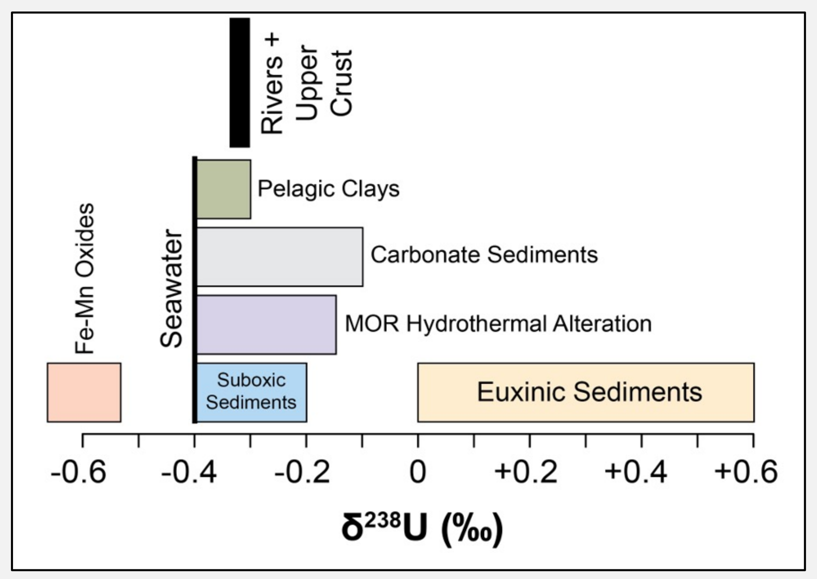


Figure 8. Mass balance model illustrating the primary sinks for seawater uranium and their isotopic compositions. Euxinic sediments represent the largest and most isotopically fractionating sink (Tissot and Dauphas, 2015).

Uranium isotopes (U) serve as a global redox proxy as uranium is soluble under oxidizing conditions, but under reducing ones, partitions into euxinic reservoirs causing isotopic redistribution. In oxic environments, uranium exists predominantly as soluble U^{6+} that stays in solution. In anoxic settings, however, U^{6+} is reduced to insoluble U^{4+}, which is sequestered in euxinic and carbonate facies and is preferentially enriched in the heavier ^{238}U isotope. Sequestration of the heavy isotope leaves seawater progressively enriched in the light ^{235}U thereby resulting in lower $\delta^{238}U$ values in carbonates.

Conclusion

The preliminary geochemical data characterized these samples with low uranium concentrations and low %TOC. The data is consistent with the broader trend observed in numerous carbonate platforms during the Middle Ordovician (Edwards, 2019). Future carbonate carbon isotope data, from the new sample set, have the possibility of reflecting the Middle Darriwilian Isotopic Carbon Excursion (MDICE), which is a positive $\delta^{13}C$ excursion. Assuming the low concentration measurements are correct, crushing extra amount of carbonate should provide enough uranium (300 ng) for the Neptune Plus ICP-MS isotope measurements. Additionally, a recent trip was made to collect additional samples, which will provide better insight into the geochemistry of the underlying Beekmantown Group and the Edinburg Formation that extends far above the initial sampling interval. These samples have already gone through sample preparation and are in the process of being analyzed for $\delta^{13}C_{carb}$, $\delta^{18}O$, and uranium concentrations. From now until fall, all 30 samples will continue to be prepared for instrument measurements, with a focus on REEs and $\delta^{238}U$ analysis. The study is on track to provide updated information by the fall and finish measurements throughout the following semester.

References/Acknowledgements

Edwards, C. T. (2019). Links between early Paleozoic oxygenation and the Great Ordovician Biodiversification Event (GOBE): A review. *Palaeoworld*, *28*(1-2), 37–50.

Kröger, B., & Lintulaakso, K. (2017). RNames, a stratigraphical database designed for the statistical analysis of fossil occurrences – the Ordovician diversification as a case study. *Palaeontologia Electronica*, 20(1). Memoir 98, p. 357 – 382.

Rey, A. D., Rasmussen, C., Calner, M., Wu, R., Asael, D., & Dahl, T. W. (2022). Stable ocean redox during the main phase of the Great Ordovician Biodiversification Event. *Communications Earth & Environment*, *3*(1).

Servais, T., & Harper, D. A. T. (2018). The Great Ordovician Biodiversification Event (GOBE): Definition, concept and duration. *Lethaia*, 51(2), 151–164.

Tissot, F., & Dauphas, N. (2015). Uranium isotopic compositions of the crust and ocean: Age corrections, U budget and global extent of modern anoxia. *Geochimica et Cosmochimica Acta*, 167, 113–143.

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