PS Constraining the Importance of Authigenic Carbonate in the Global Carbon Cycle: A Case Study From the Bakken Formation*

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Abstract

The Late Devonian is characterized by several important environmental perturbations and includes the Hangenberg event, characterized by a mass extinction, marine anoxia, and a ~+5‰ positive carbon isotopic excursion (+CIE) in marine carbonates. The Hangenberg is also associated with the global occurrence of black shale deposits. Recent work has hypothesized that authigenic carbonates, often formed diagenetically during the remineralization of sedimentary organic matter, are a volumetrically significant and isotopically depleted sink for carbon, and thus important for interpreting the environmental implications of isotopic records. Because black shales are a likely host for authigenic carbonates, it is possible that the Hangenberg +CIE was driven by increased rates of organic carbon and authigenic carbonate burial, a model that has not yet been treated quantitatively. Here we estimate the mass and isotopic composition of carbonates in the Upper Devonian-Lower Mississippian Bakken Formation. Powdered samples were collected from three cores covering the Williston Basin depocenter and margin and were analyzed for bulk mineralogical and stable carbon and oxygen isotopic composition. Carbonates represent a significant mass within the unit – the Lower and Upper black shale members are, on average, ~9 wt.% authigenic carbonate and the Middle member calcareous siltstone is ~48 wt.% carbonate, of which approximately 60% is detrital grains and 40% is carbonate cements. Carbon isotopic measurements from gas-source mass spectrometry range from -6.5‰ to +3.9‰ (VPDB). The basin center and basin margin cores show a positive $\delta^{13}C$ shift of +3.0‰ and +3.3‰, respectively, from the Lower Black shale into the Middle siltstone. This positive excursion may reflect the Hangenberg +CIE. However, the basin center core yields $\delta^{13}C$ values that are isotopically lighter by approximately 2‰ relative to the basin margin core. There is also a weak negative correlation between TOC and $\delta^{13}C$, suggesting that authigenic carbonate produced from remineralized organic matter is mixing with marine carbonate to cause systematic but small negative offsets in the $\delta^{13}C$ of the basin center relative to the basin margin. Thus, authigenic carbonates in Late Devonian black shales are unlikely to be a strong lever for driving positive isotopic shifts in the carbon isotopic composition of seawater, but they remain a significant sink for inorganic carbon that must be considered in global carbon cycle models.

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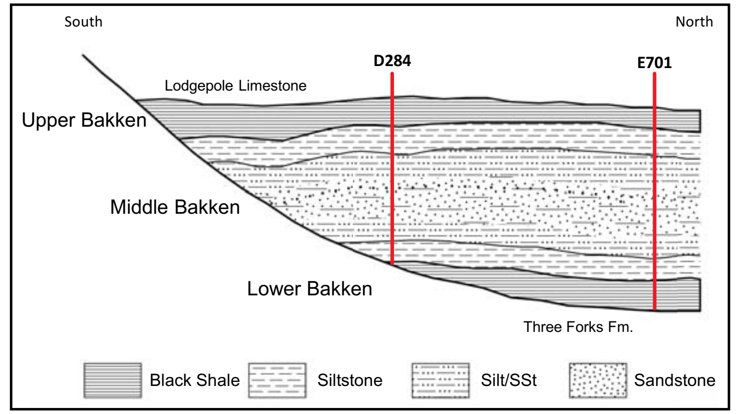
Here we estimate the mass and isotopic composition of carbonates in the Upper Devonian-Lower Mississippian Bakken Formation. Powdered samples were collected from three cores covering the Williston Basin depocenter and margin and were analyzed for bulk mineralogical and stable carbon and oxygen isotopic composition. Carbonates represent a significant mass within the unit – the Lower and Upper black shale members are, on average, ~9 wt.% authigenic carbonate and the Middle member calcareous siltstone is ~48 wt.% carbonate, of which approximately 60% is detrital grains and 40% is carbonate cements. Carbon isotopic measurements from gas-source mass spectrometry range from -6.5‰ to +3.9‰ (VPDB). The basin center and basin margin cores show a positive $\delta^{13}C$ shift of +3.0‰ and +3.3‰, respectively, from the Lower Black shale into the Middle siltstone. This positive excursion may reflect the Hangenberg +CIE. However, the basin center core yields $\delta^{13}C$ values that are isotopically lighter by approximately 2‰ relative to the basin margin core. There is also a weak negative correlation between TOC and $\delta^{13}C$, suggesting that authigenic carbonate produced from remineralized organic matter is mixing with marine carbonate to cause systematic but small negative offsets in the $\delta^{13}C$ of the basin center relative to the basin margin. Thus, authigenic carbonates in Late Devonian black shales are unlikely to be a strong lever for driving positive isotopic shifts in the carbon isotopic composition of seawater, but they remain a significant sink for inorganic carbon that must be considered in global carbon cycle models.

Study Site

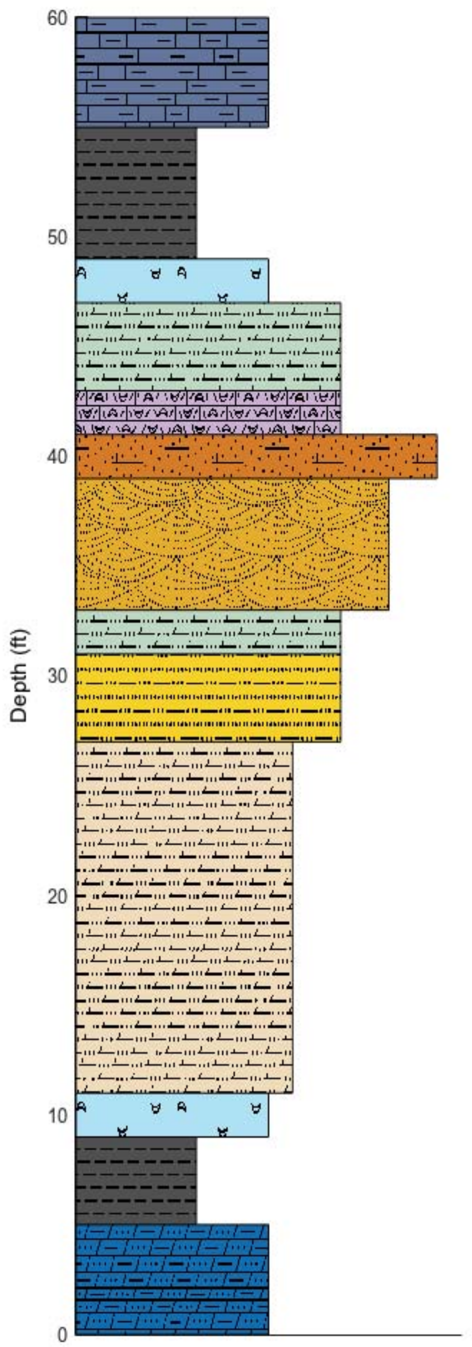
Lithologic and geochemical data from the Bakken was compiled from the USGS Core Research Center (CRC). Two of the cores housed in the Denver CRC were then chosen for further study: basin-central E701 and basin-marginal D284.

A Late Devonian paleogeographic map showing Laurentia and the location of the Williston Basin during early deposition. Paleolatitude is ~10°S (modified from Blakey, 2011).

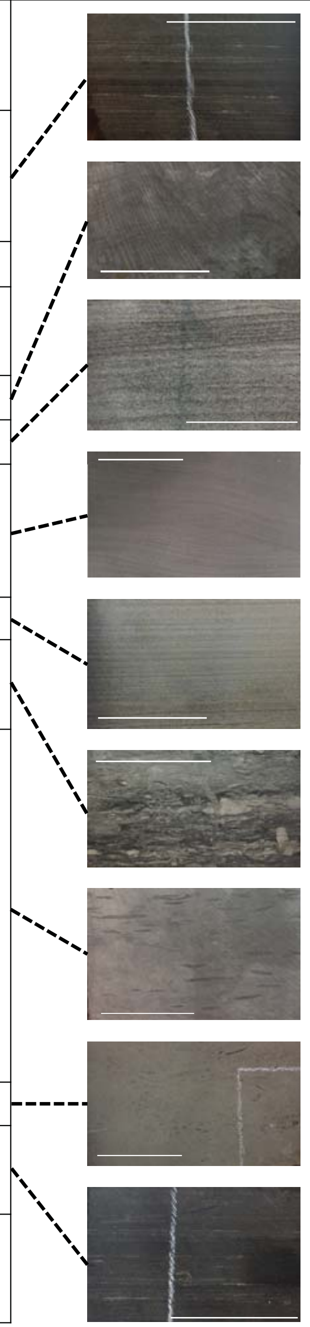
Modern map of the Bakken Fm. boundaries in North Dakota and Montana, detailing structural features and the location of cores studied (modified from Gaswirth et al., 2013).



Stratigraphic cross-section of the onlapping Bakken Fm and adjacent units; the approximate basinal position of study cores are marked in red (modified from Kuhn, 2012).



Facies (after Egenhoff et al., 2011)	Core Sample	Thin Section
Lodgepole Limestone		
F1. Upper Bakken Shale		
F11. Carbonate Wackestone		
F6. Sandy Siltstone		
F9. Laminated Bindstone		
F8. Quartz Sandstone with Ooids		
F7. Cross-Bedded Sandstone		
F6. Sandy Siltstone		
F4. Intercalated Sand/Siltstone with Mudstones		
F3. *Nereites* Siltstone		
F11. Carbonate Wackestone		
F1. Lower Bakken Shale		
Three Forks Fm		

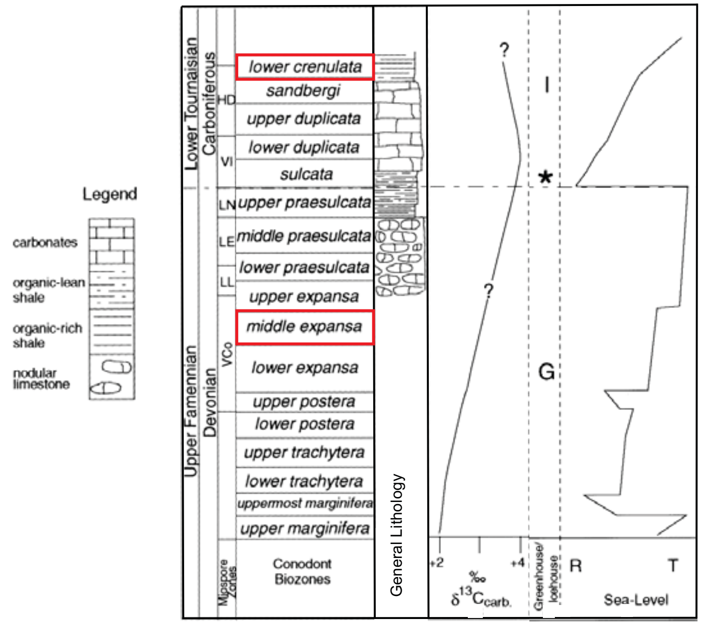


Generalized Bakken stratigraphic column, with facies details, typical core samples, and petrographic thin section photos. White bars in core photos measure 1cm.

Hangenberg Event

The End-Devonian Hangenberg Event can be correlated by the global deposition of organic-rich black shales in an anoxic ocean setting. It is also marked by a mass extinction and regression, attributed to glaciation and eutrophication.

A positive carbon isotopic excursion with ~+2–5‰ magnitude occurs in the Hangenberg as well. Given the preceding extinction of reef-building calcifiers and black shale deposition, this excursion is interpreted to be the result of isotopically-depleted, organic carbon burial driving a positive secular shift in the oceans. In addition to indicative fossils, this trend can be used to correlate Hangenberg Black Shales (HBS). In the absence of either, the Bakken Fm has been only questionably labeled as an HBS.

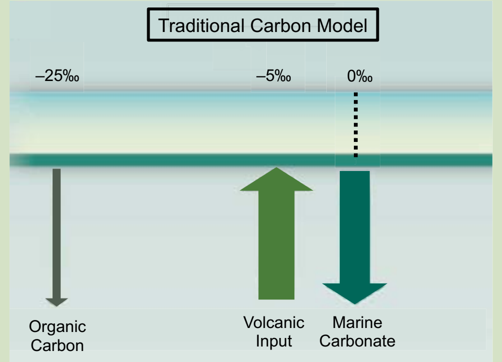


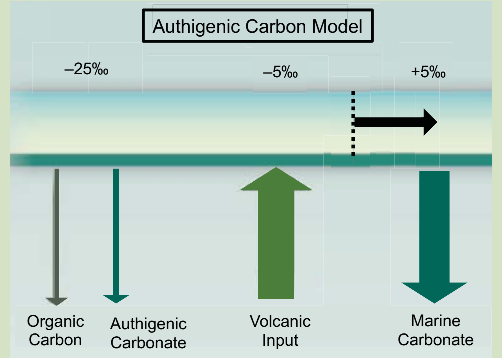
Modified from Caplan and Bustin, 1999. Red boxes mark the upper and lower bounds of Bakken shale members' conodont biostratigraphy.

Authigenic Carbonates

The traditional global carbon cycle model incorporates two sinks: isotopically-light organic carbon, and heavy marine carbonate. Over geologic time scales, the two sinks balance volcanic input of mantle carbon. Recently, Schrag et al. (2013) proposed authigenic carbonate – precipitated *in situ* – as an important third sink. Because authigenic carbonates can form from remineralized organic carbon, they can also be isotopically light, and potentially force marine carbonate to heavier values in excursions.

This model can be better understood by estimating authigenic carbonate mass and $\delta^{13}C$ in times of high organic burial, redox dominating oceans, and a sudden positive isotopic excursion. In order to test this for the Hangenberg event, the Bakken Fm will be used as a case study.





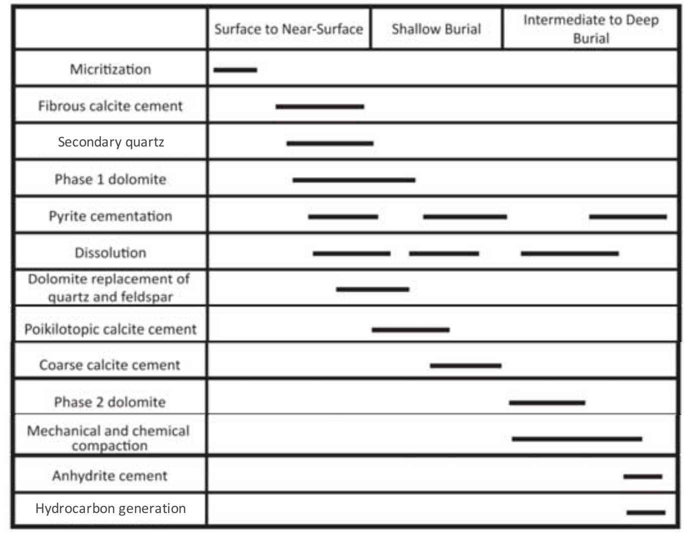
Modified from Canfield and Kump, 2013

Bakken Diagenesis

Diagenetic carbonates make up a significant portion of the Bakken Fm, particularly within the Middle Bakken. Of the ~48 wt% carbonate, on average 30–45 wt% is made up of cements and dolomitization replacement (Staruiala, 2015). Calcite cements occur as well, both typically forming in early-to-mid diagenetic stages.

Despite the high volume of authigenic carbonates in the Middle Bakken, bulk $\delta^{13}C$ values are closer to marine values than in the shales. This is likely due to the early formation of cements, rather than large rims forming during hydrocarbon maturation and migration.

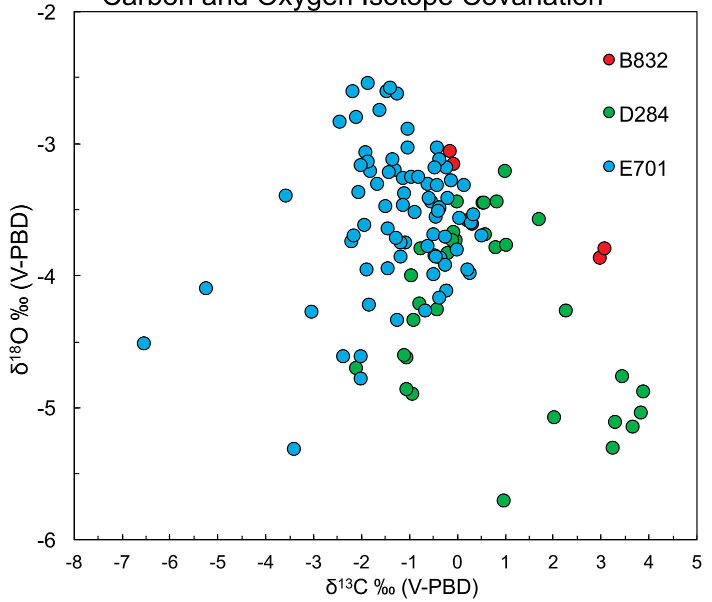
While the carbonate content of the shale members is predominantly authigenic dolomite, the bulk values are not as light as organic carbon. This suggests a more nuanced role of authigenic carbonate formation in the global carbon cycle.

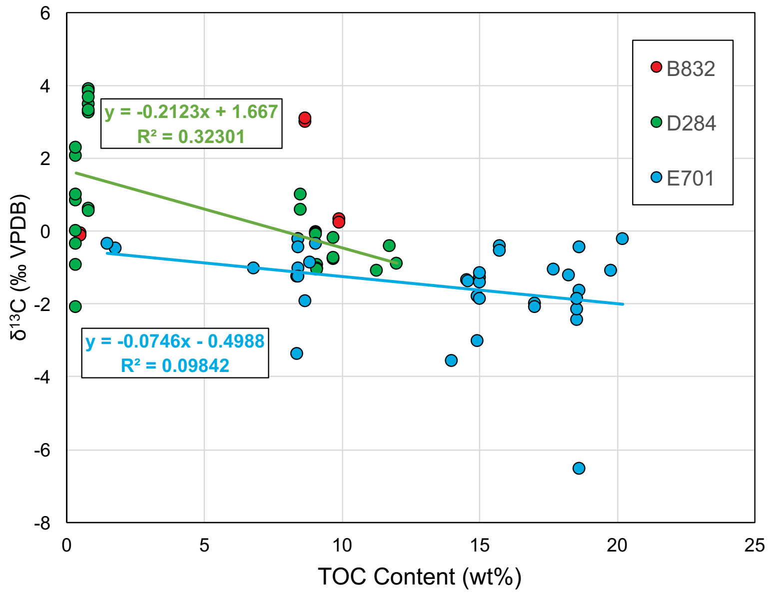


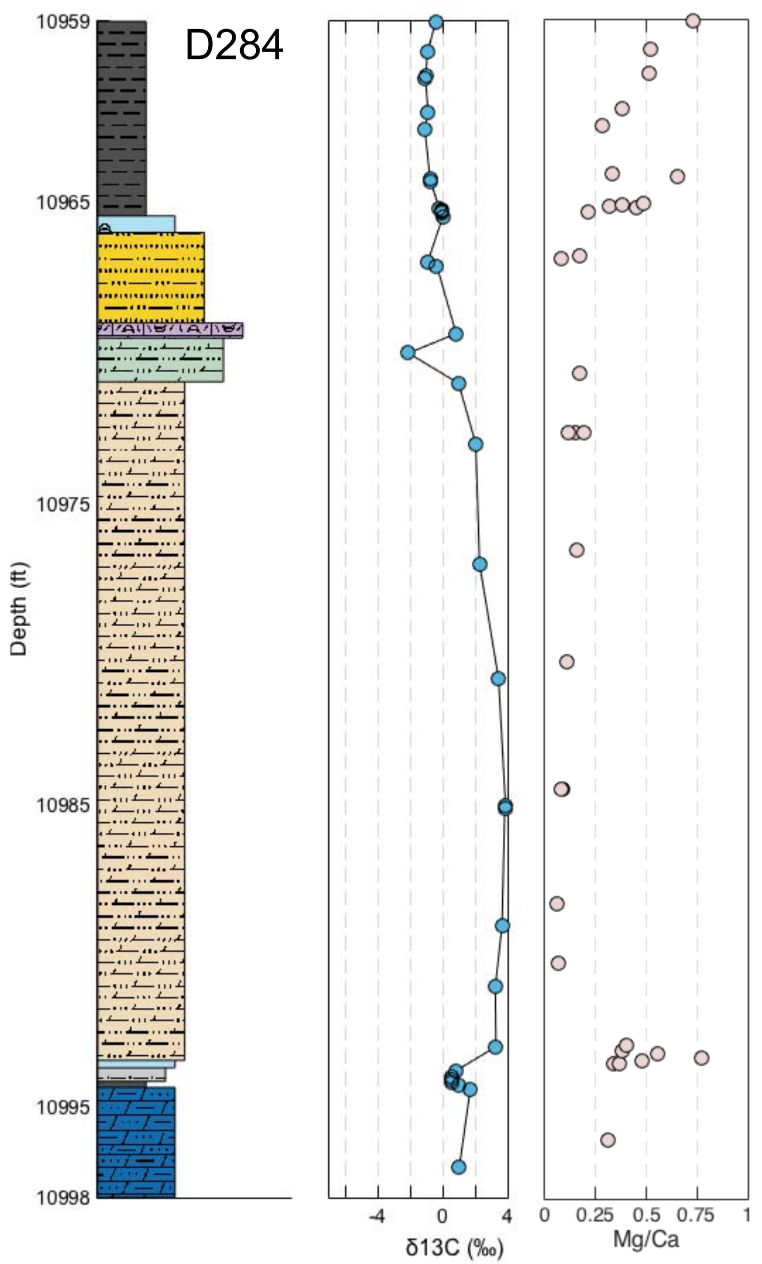
Modified from Staruiala, 2015

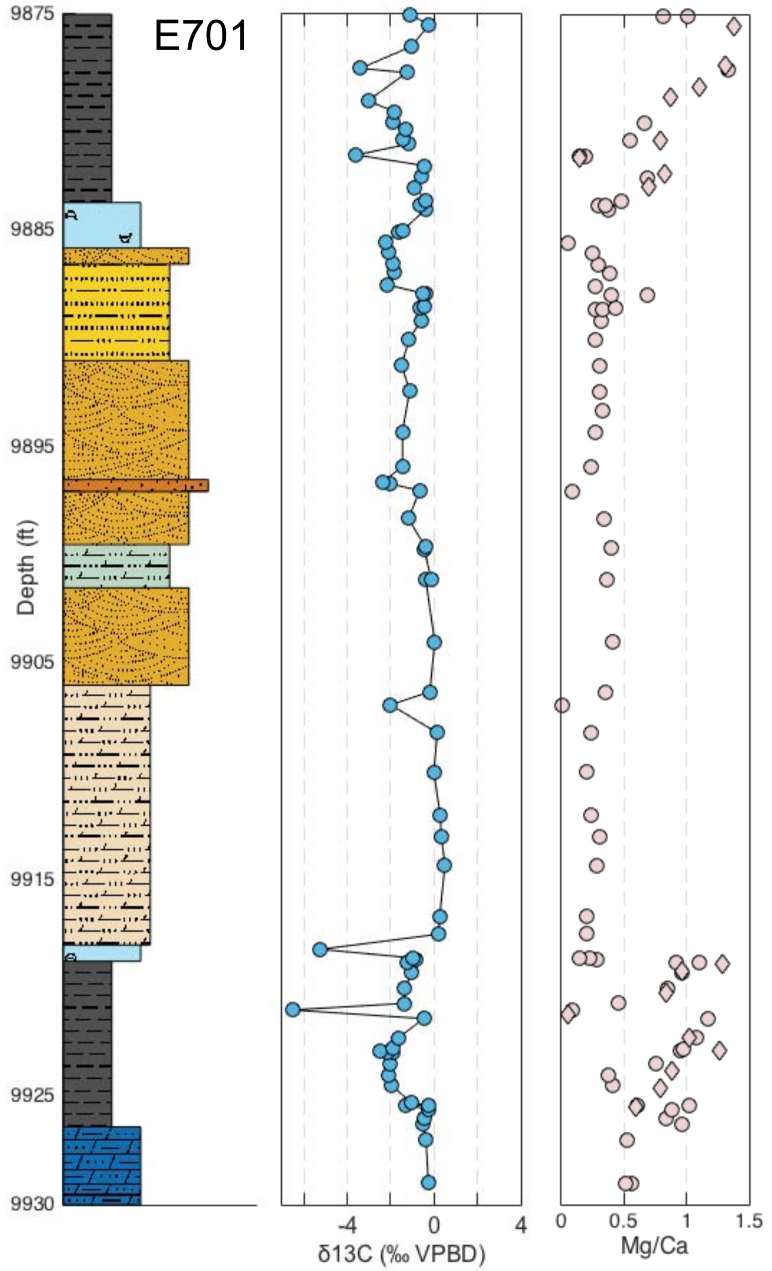
Covariation between carbon and oxygen isotopic data is a common indicator of meteoric diagenesis overprinting: however, the cross plot below does not show the expected strong, positive correlation associated with this diagenesis.

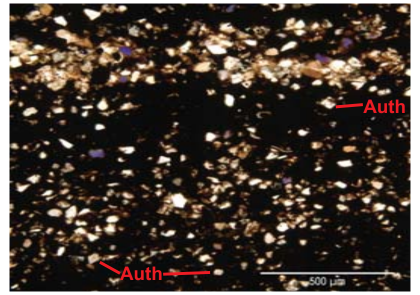
A weak negative relationship exists between TOC and $\delta^{13}C$: this may be due to increased chance of organic carbon recrystallization in areas of high TOC, yielding isotopically lighter authigenic carbonate.



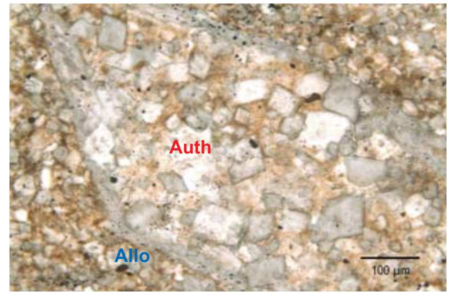




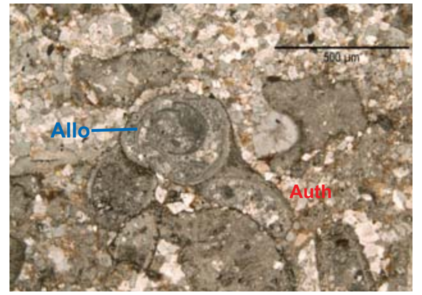




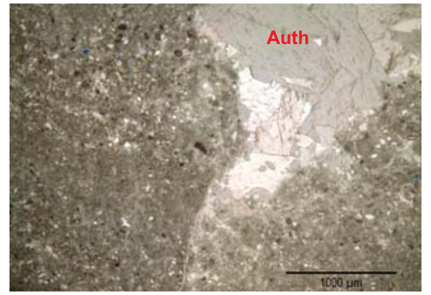
F1. Disseminated auth. dolomite rhombs



F11. Allogenic macrofossil with auth. dolomite rhombs and recrystallization



F6. Reworked allogenic ooids and bioclasts with cements

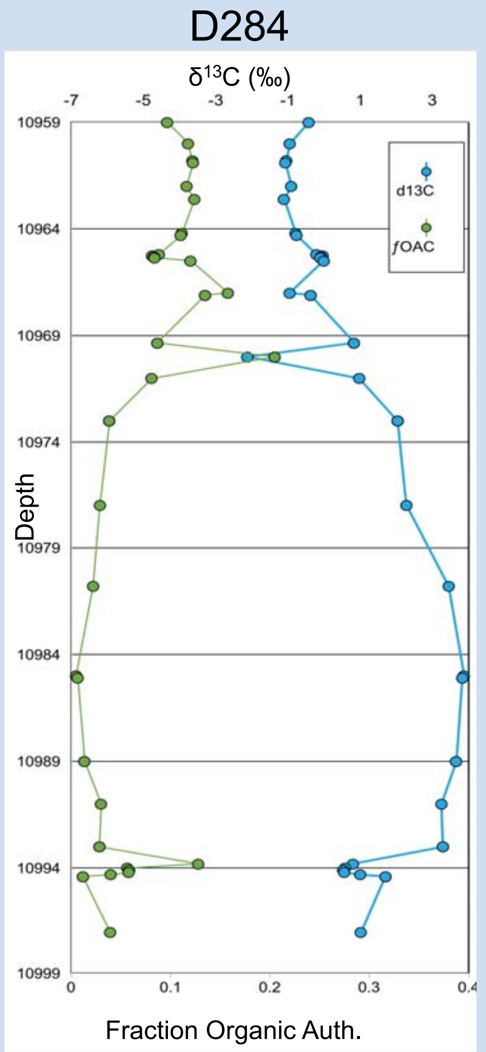


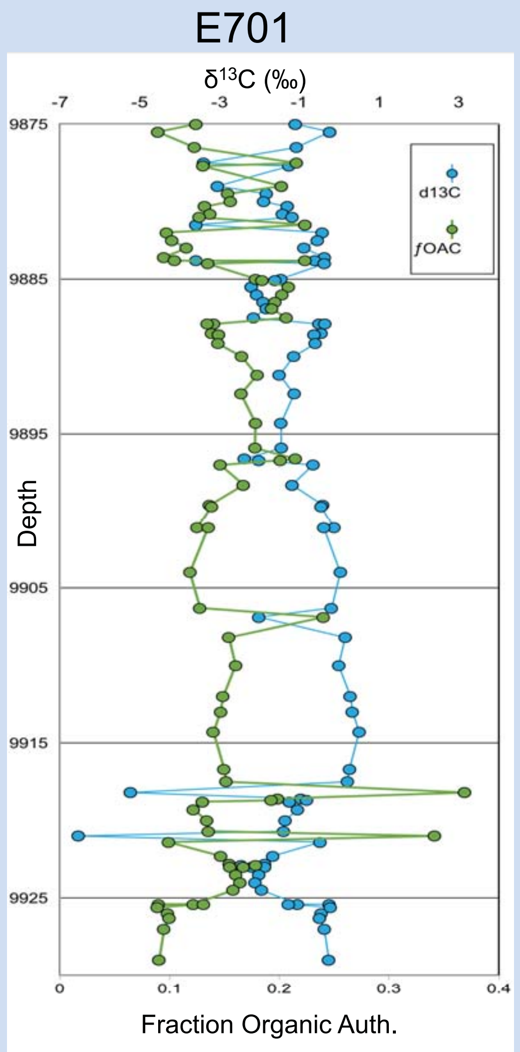
F9. Carbonate silt stromatolite bindstone with calcitic fenestra.

Conclusions and Future Work

The Bakken Formation shales exhibit a high authigenic carbonate volume expected from an anoxic period rich in organic deposition. Because of the control of paleodeposition site and TOC content on carbonate content, it is clear that the authigenic carbonate component must be estimated on a formation-scale in order to gain a full understanding of the global carbon cycle during times of perturbation. Our bulk measurements also provide evidence for the Hangenberg Excursion being contained within the Bakken, aiding in correlation to the global occurrence of Hangenberg Black Shales.

Contrary to Schrag et al.'s model, we find that the isotopic composition of carbonates is an admixture of light organic carbon and heavier marine precipitated carbonate. As can be seen in the below, even low proportions of organically-derived authigenic carbonates can account for the difference between canonical ocean values and the Bakken bulk rock $\delta^{13}C$. The carbonate crisis caused by the extinction of reef-building organisms and redox environment may also promote inorganic carbonate precipitation on the seafloor. While authigenic carbonates do play a role in the global carbon cycle, further formation-level studies will be necessary to fully understand how they affect positive isotopic excursions.

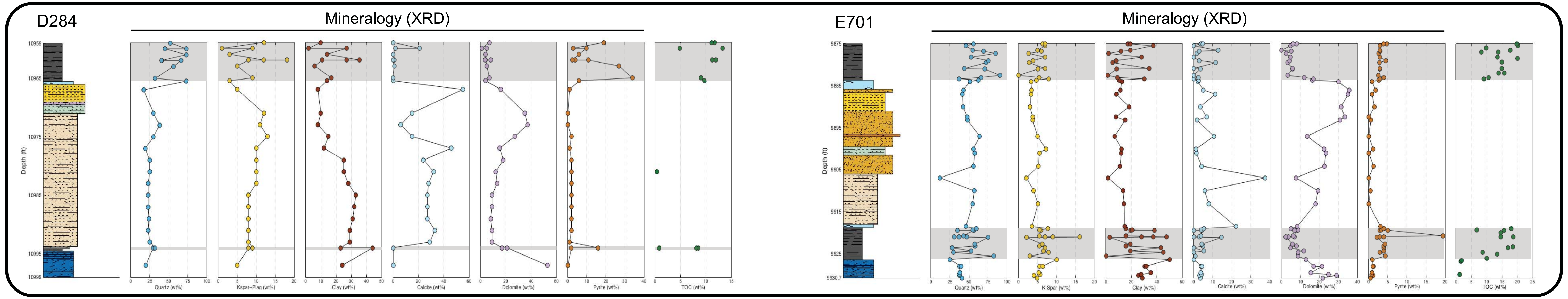




Member	TOC[1]	Quartz[2]	K-Spar[2]	Calcite[2]	Dolomite[2]	Pyrite[2]	Clays[2]	Anhydrite[2]
UBS	10.59 (326)	50.40 (166)	7.93	1.44	8.83	6.52	21.8	0.03
MB	0.49 (371)	28.33 (73)	5.05	14.77	32.84	1.16	14.84	1.06
LBS	9.15 (314)	44.59 (68)	9.81	1.12	5.64	6.71	29.89	0

Mineralogical and geochemical data compiled from the USGS CRC are summarized above. Headings marked with [1] are in weight % from LECO–TOC measurements, while those with [2] are weight % from XRD analyses. Sample sizes are given in parentheses.

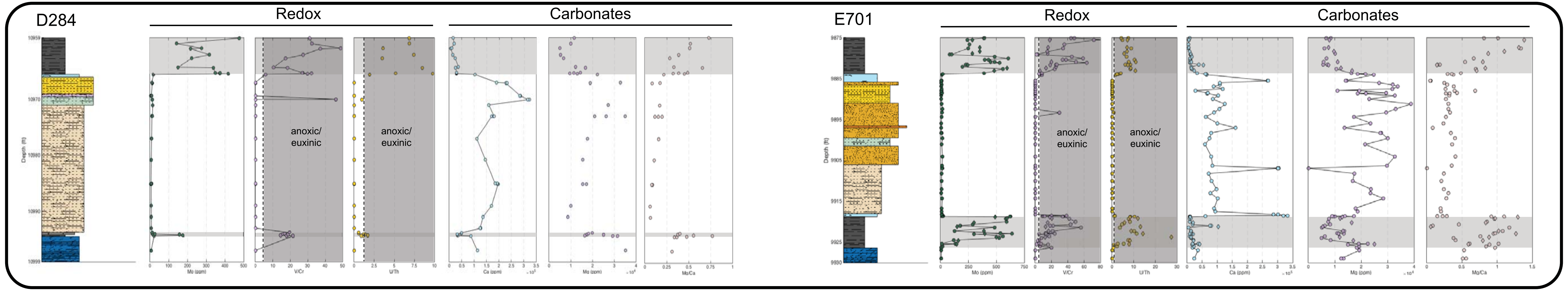
The data show that the Upper and Lower shale members are generally similar: rich in quartz and clays, but bearing significant dolomite mass as well. In contrast, the Middle Bakken silt-sandstone is predominantly carbonate (calcite and dolomite), with lesser proportions of quartz and clay.



The remaining proxies were measured using sampled powders with a mounted Thermo Fischer Niton Handheld XRF (120 seconds each sample) at the Wisconsin Geological and Natural History Survey. Data were calibrated using USGS standards. Data illustrated as diamonds come from Scott et al., 2017 (WD–XRF and ICP-MS) as comparison of instrument precision.

Proxies for redox environment and ocean anoxia/euxinia show greater prevalence in the basin-central E701 core. V/Cr and U/Th as indicators of anoxia/euxinia were calculated after Jones and Manning, 1994.

Carbonate XRF proxy data correlates with the XRD mineralogical curves, and underline the relative abundance of dolomite over calcite within the shales. The Mg/Ca curve as a proxy for dolomite (and illite) covaries with redox proxies, suggesting a diagenetic control for carbonate in the black shale members. Euxinia/anoxia promote burial of organic carbon and aerobic respiration by iron- and sulfate-reducing bacteria, which in turn promotes the remineralization of organic carbon to authigenic carbonates.



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Acknowledgements

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