

# **PS Identification of Triggers for Organic Matter Burial of the Middle and Upper Devonian Horn River Shale, Northeastern British Columbia, Canada\***

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## **Abstract**

Organic richness in black shales is directly related to the oil and gas generation. Organic matter (OM) enrichment in turn is mainly controlled by a combination of productivity, redox conditions, and dilution. These factors have multiple influences on organic matter accumulation. However, interplays or feedback loops between productivity and redox controls result in proxies for these parameters varying synchronously in many formations, for example such that shifts to both higher bioproductivity and more anoxic conditions may be indicated at points in a shale section where TOC increases. At the scale we commonly sample drilled cores, it is typically impossible to resolve what factor triggers organic carbon enrichment. In this study, we are building a high-resolution geochemical dataset of the Horn River Shale, Western Canada Sedimentary Basin. The geochemical dataset includes high-resolution inorganic geochemical analyses by benchtop EDXRF and high-resolution TOC analyses by hyperspectral imagery, supplemented and calibrated by whole rock geochemical analyses by ICP-MS and Leco TOC analyses. To analyze the interplay between productivity and redox conditions, sampling resolution should reflect the time lag corresponding to the reactions that describe feedbacks, for example when enhanced bioproductivity induces bottom water anoxia. The lag duration may be tens to hundreds of years, which can correspond to millimeters of vertical section due to the low sedimentation rate in shales. The benchtop EDXRF collected inorganic geochemical data with 1 mm ~ 2 mm resolution and total organic carbon (TOC) was measured by hyperspectral imagery with 0.5 mm resolution, corresponding to approximately 31 yr ~ 85 yr and 16 yr ~ 20 yr respectively in the Horn River Shale.

Geochemical analysis indicates the three stratigraphic units, the Evie Member, Otter Park Member, and Muskwa Formation, were characterized by diverse dilution, redox conditions, and bioproductivity. Carbonate input is common in the Evie Member and terrigenous input (aluminum concentration) is richer in the Otter Park Member, while the Muskwa Formation has the highest bioproductivity due to the high biogenic silica content. We apply biogenic silica and S/Fe ratio as proxies for productivity and redox conditions respectively. Examples include increases in S/Fe followed upward with a several-millimeter lag by increased biogenic silica suggesting that anoxia may have enhanced bioproductivity probably. In other examples, increased biogenic Si followed upward by increased S/Fe indicates organic content decay causes oxygen depletion in the bottom water. Our results provide the evidence for the interplay between productivity and redox conditions and identify triggers among productivity, redox conditions, and dilution for OM accumulation in different intervals of the Horn River Shale.

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## Methods

### Proxies:

**Dilution:** Al (detrital flux) and Ca (carbonate flux);

**Bioproductivity:** biogenic silica;

**Redox conditons:** Mo/Al and S/Fe (S/Fe < 0.3 – oxic; 0.3 < S/Fe < 0.42 – dysoxic; 0.42 < S/Fe < 1.15 – anoxic);

**OM burial:** TOC ( $R_o$  1.6% - 2.5%).

### Approaches:

#### Benchtop EDXRF

1 mm - 2 mm vertical resolution;

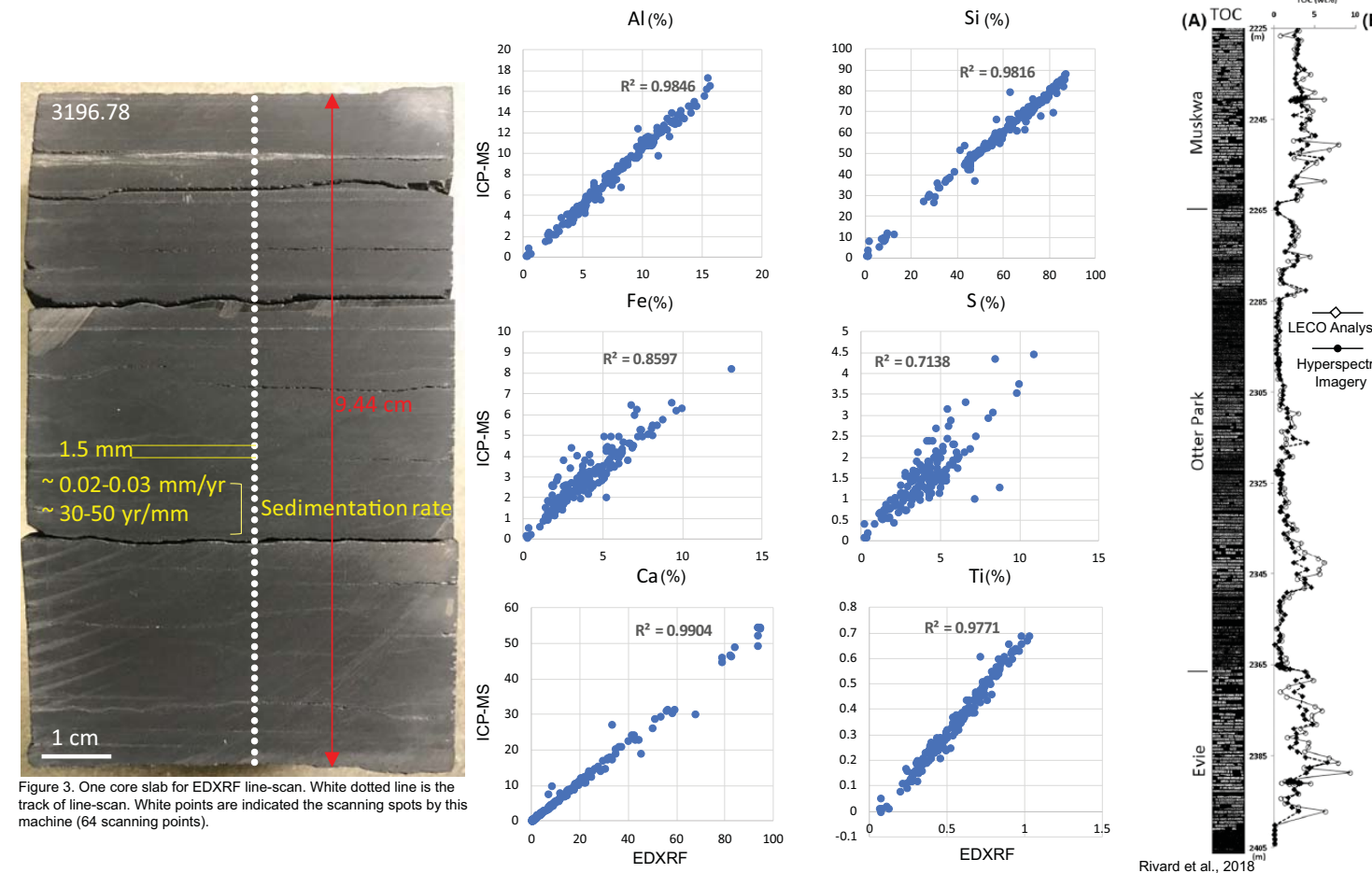
Elements: Mg, Ca, Si, Al, S, Fe, K, Ba, and Ti (0.01% detection limit).

#### Hyperspectral imagery (infrared scan)

0.8 mm – 1.5 mm vertical resolution;

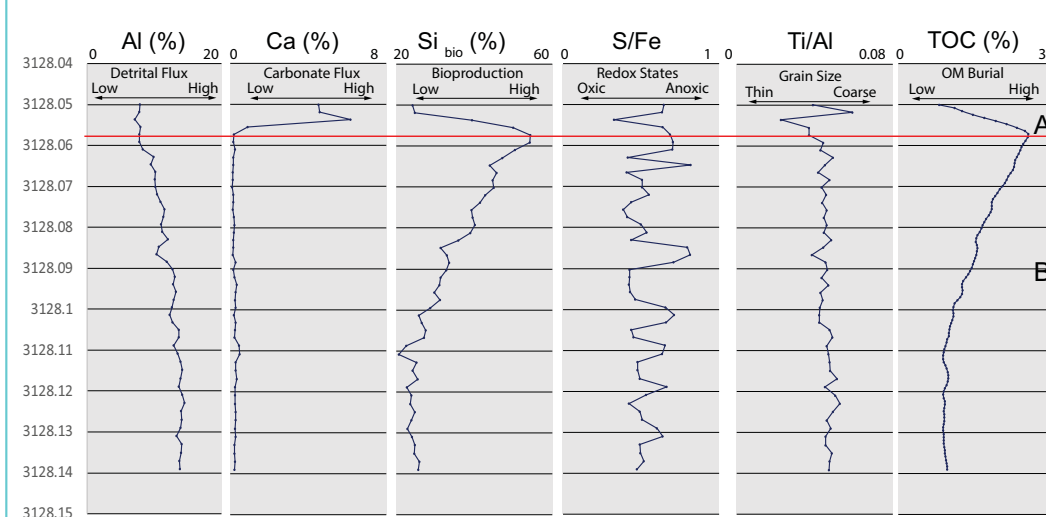
Geochemical components: TOC (total organic carbon) and  $SiO_2$ .

#### ICP-MS and LECO analyses (calibration)



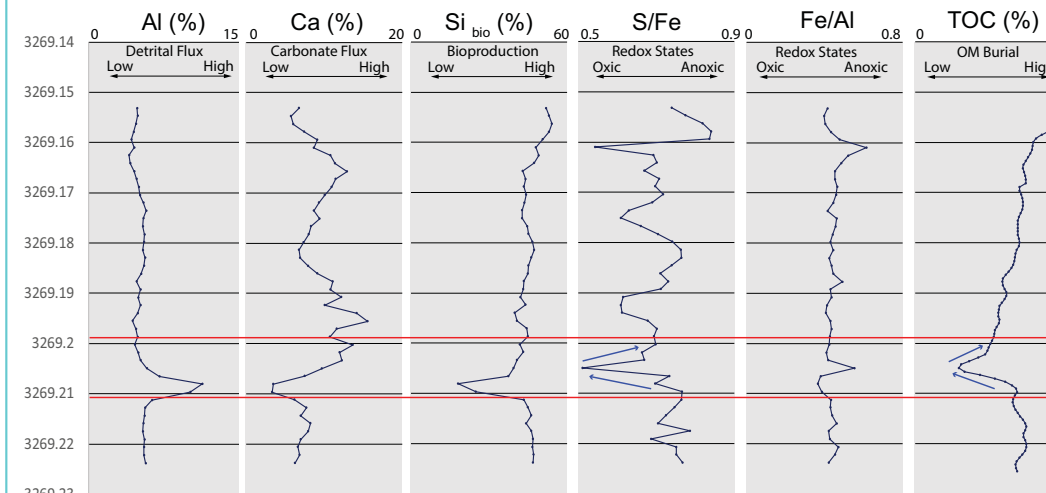
## Results

### Bioproductivity Triggers OM Burial



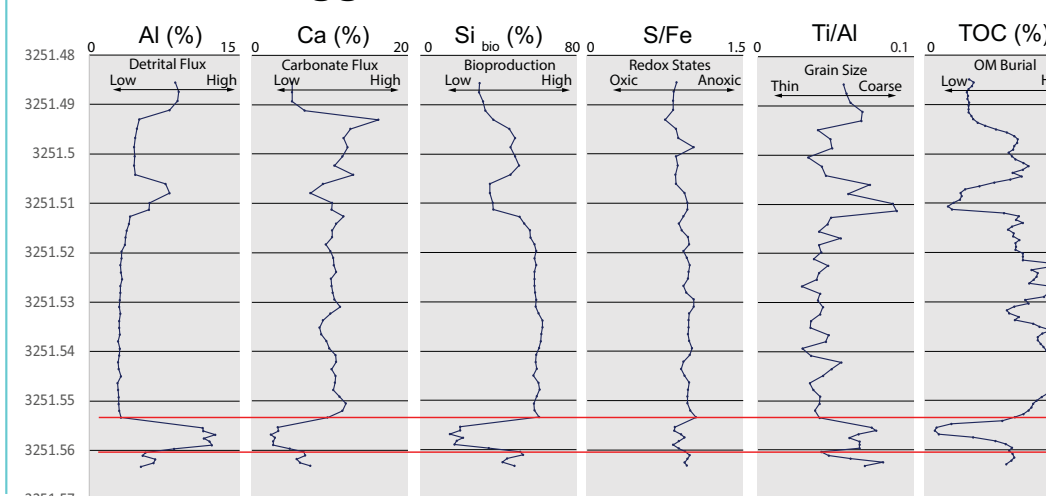
$Si_{bio}$  (biogenic silica)/TOC ratio is 26.1 - 28.5 in the whole interval. Variable S/Fe ratios decoupled from TOC indicates oscillating redox states, but redox has less influence than bioproduction on OM burial. In A interval, sediment source changes into reefs indicated by Ca, but  $Si_{bio}$ /TOC is still stable, so actual trigger is bioproduction.

### Redox Conditions Trigger OM Burial



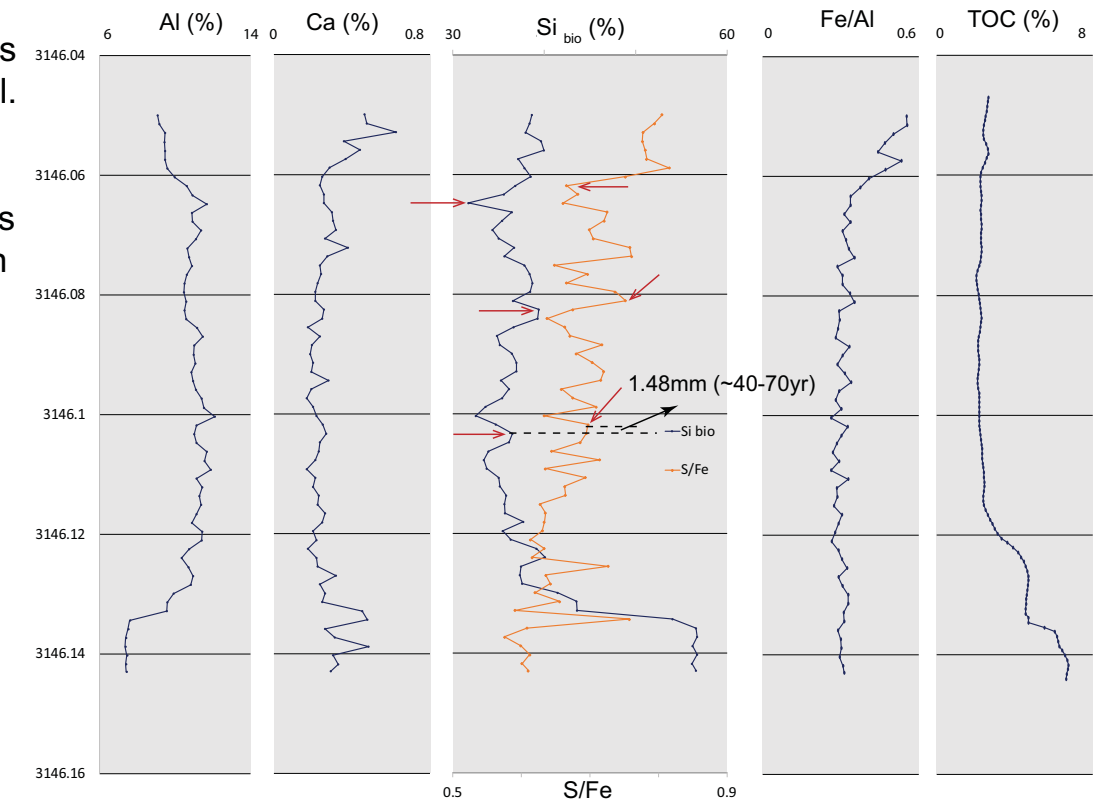
Between red lines, TOC tracks consistently with S/Fe. Al also reaches maximum with decreased Ca and  $Si_{bio}$ , indicating increased detrital inputs. However, the depth of Al, Ca, and biogenic Si peaks is 3.1 mm lower than depth of TOC and S/Fe peaks, so the actual trigger for OM burial is redox states.

### Dilution Triggers OM Burial



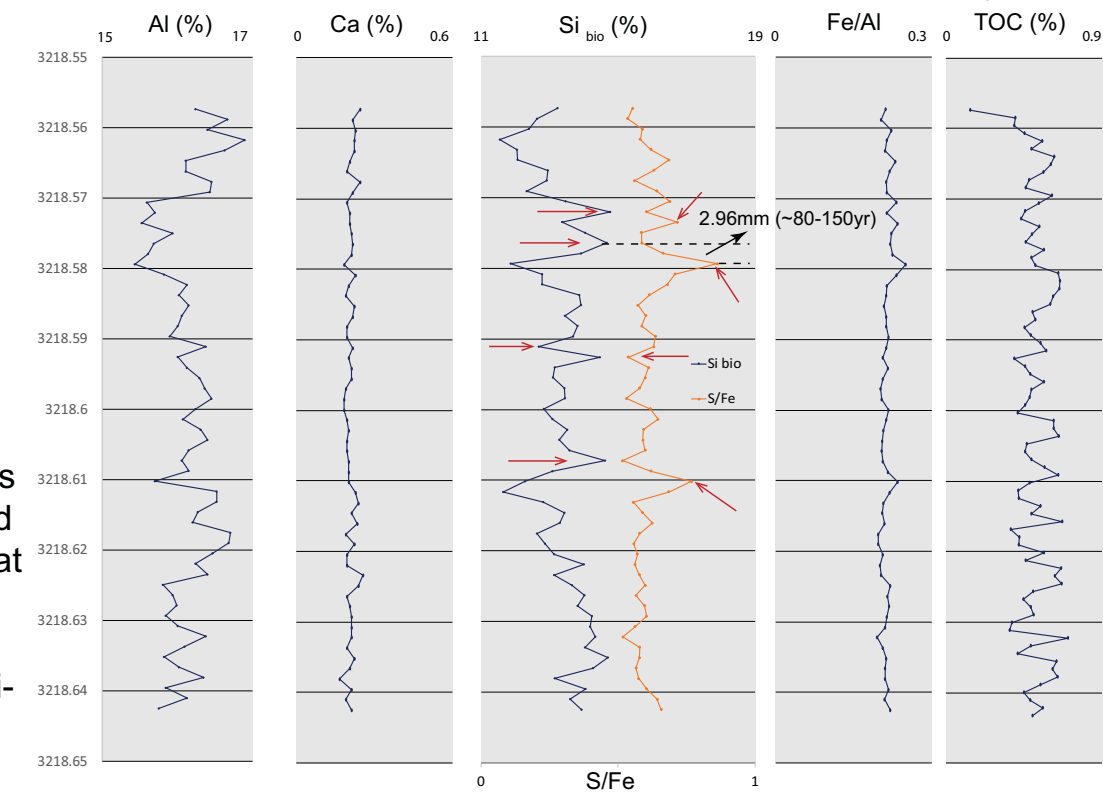
Between red lines, ratio between  $Si_{bio}$  and Ca is 6 - 7, reflecting stable carbonate and  $Si_{bio}$  inputs, but  $Si_{bio}$ /TOC ratios change from 12 to 29, coupled with Ti/Al and Al, indicating that  $O_2$  by increased detritus decomposes OM by oxidation. The trigger for OM burial is dilution in this interval.

### Bioproductivity influences redox conditions



Indicated by red arrows, biogenic silica changes 1.48mm ahead of S/Fe in some intervals, equivalent to ~40-80 yr. This lag period reflects the feedback between bioproduction and redox terms. The trigger of this interplay is bioproductivity.

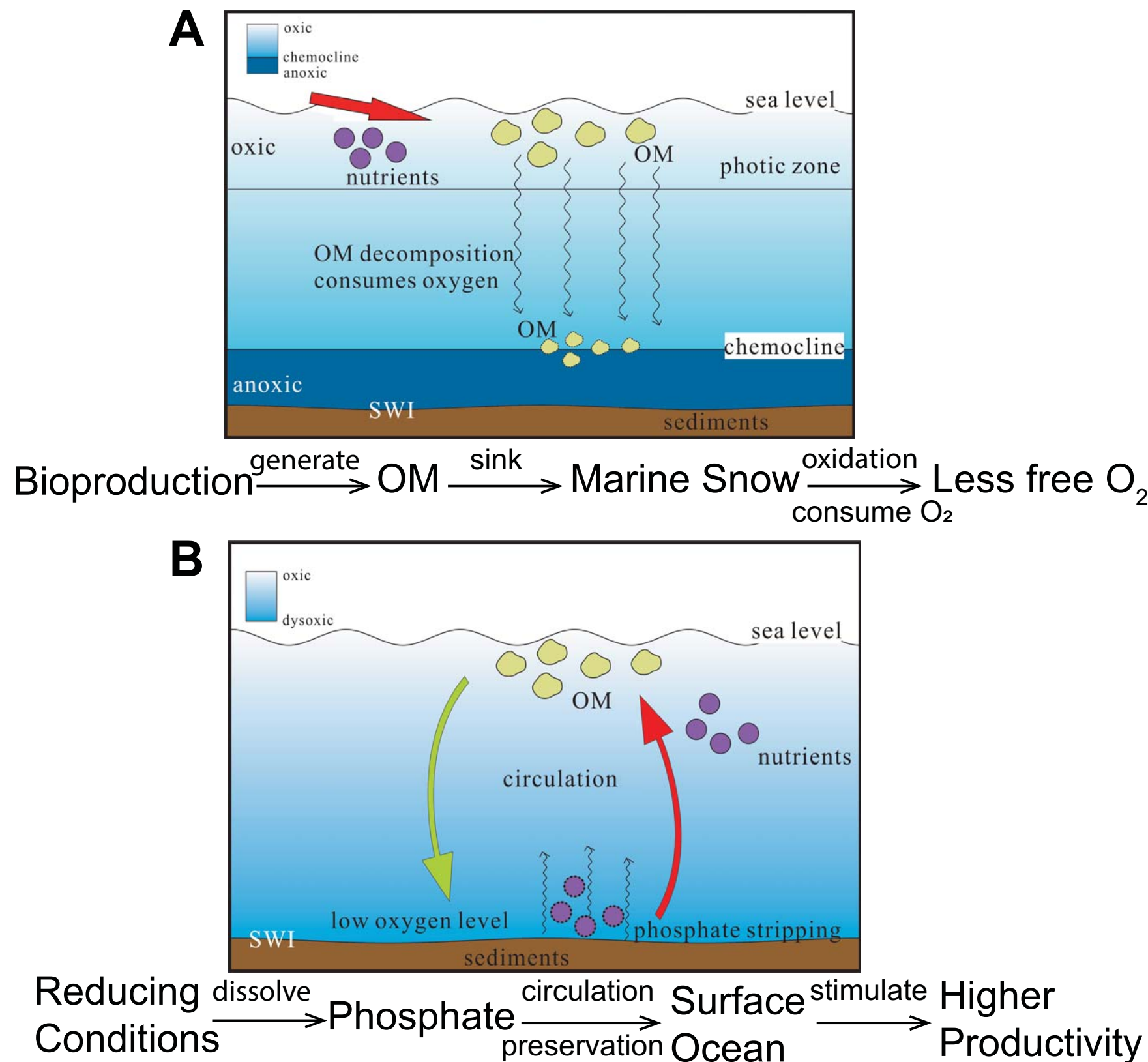
### Redox conditions influence bioproductivity



Indicated by red arrows, biogenic silica changes 2.96mm above S/Fe in some intervals, equivalent to ~90-150 yr. This lag period reflects the redox-bioproduction feedback. Redox states in turn trigger this feedback loop.



## Feedback Models



## Interpretation of Horn River Basin

138 samples are valid. Triggers for OM burial and redox-bioproductivity feedbacks are various in different stratigraphic units:

### Trigger for OM burial

**Dilution:** Otter Park Member (FSST, HST, LST), Evie Member (HST);

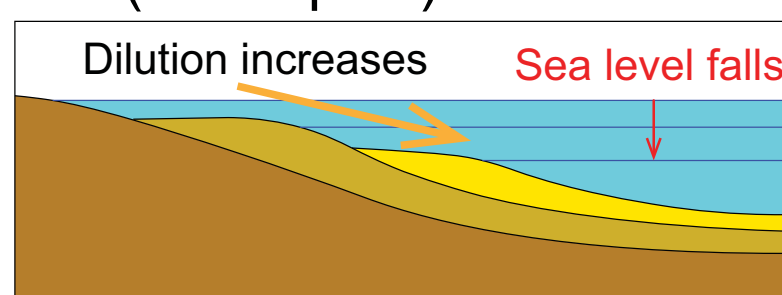
**Bioproductivity:** Evie Member (TST), Muskwa Formation (TST, HST);

**Redox conditions:** Rare, mostly in TSTs (6 samples).

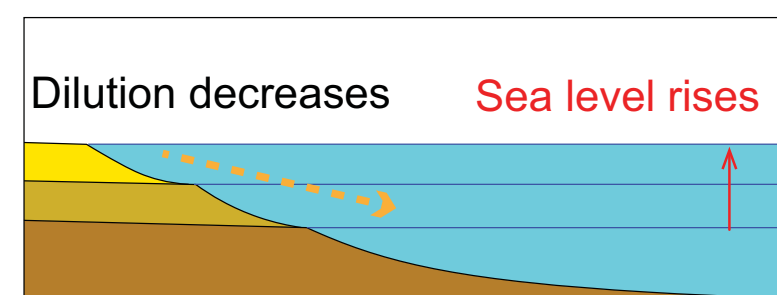
### Feedback Patterns

**Bioproductivity-start feedback (A):** Evie Member (TST) and Muskwa Formation (TST);

**Redox-start feedback (B):** Rare, in HST (2 samples) and TSTs (2 samples).



Falling sea-level can increase detritus effect in deep-ocean muds and influence oxygen level on seafloor and biogenic silica concentration.



Rising sea-level weakens dilution, converting ternary system to binary system. Thus, feedbacks of anoxia and production are easier to be identified.

## Conclusions

1. Bioproductivity, redox controls, and dilution have various influences on the Horn River Shale indicated by variations in their proxies.

2. At some sections, oxygen depletion is decoupled from bioproduction. Relative sea level change or climate may influence redox states by changes of sedimentation rate.

3. In some intervals, under high productivity or reducing environment, changes of terrigenous inputs may also influence OM burial.

4. Oxygen level is associated with bioproductivity because of redox-bioproduction feedback loops (~40-150 yr) by lags between geochemical indicators (S/Fe-Si<sub>bio</sub>).

5. Within TSTs, redox-bioproduction feedbacks are mostly observed because of less dilution effects.

6. Such feedbacks also reflect water-mass stratification-mixing cycles.

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