Early diagenetic controls affecting the inorganic composition of oil shale from the upper Green River Fm. (Mahogany Oil Shale Zone — Uinta Fm. boundary), Uinta Basin, Utah

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OUTLINE

1. Uinta Basin sedimentology & stratigraphy
2. Field Methods
3. ICP
4. XRD
5. SEM
6. Models
7. Summary
1. Uinta Basin sedimentology & stratigraphy

- Duchesne River Formation
- Uinta Formation
- Horsebench sandstone bed
- Mahogany oil shale
- Sunnyside delta facies
- Douglas Creek Member
- Flagstaff Formation
- North Horn Formation
- Green River Formation

- ~ 300m
- ~50km

- Cowboy Buck Gate
- Duchesne
- Price

- Department of Geology University of New Brunswick
2. Field Methods

- main sampling every 4m,
- ...plus tuff & all outcropping oil shale
- ICP (all samples), XRD & SEM (selected)
2. Field Methods
3. ICP
Buck (measured):
Phosphorus anomalies in some oil shale
- P abundance correlates positively (significance level, $\alpha = 0.01$) with U, Th, Sr
  & with REEs (particularly heavier REEs)

![Graph showing phosphorus, thorium, uranium, and strontium levels across different depths.]

Crystallized bed
@ 128.2 m = 6.3% (2 replicates)
3. ICP Buck (measured):
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Note: Normalized against PAAS; box-whiskers for ALL samples
- Average values plot close to USGS SGR-1 reference sample
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Correlation to other sections?

-all exposed oil shale beds sampled @ Gate (& Cowboy): possible matches
4. XRD
Buck:

Confirms phosphorus anomalies in some oil shale

*Note: shales mostly marly – minimal clays*

<table>
<thead>
<tr>
<th>Sample Horizon</th>
<th>Lithofacies</th>
<th>Quartz</th>
<th>Feldspars</th>
<th>Sheet silicates</th>
<th>Calcite</th>
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*Note: P confined to top ~ 5cm of oil shale*
4. XRD

Buck:

Confirms phosphorus anomalies in some oil shale
- As calcium fluorapatite (CFA), e.g. 128.2m
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Confirms phosphorus anomalies in some oil shale
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5. SEM
Buck:
Early diagenetic phase in calcite laminae
(pre-compaction & organic degradation)

Algal (?)Pediastrum) or substrate coccoid bacteria?

Calcite platelets (?) Calc green algae

UNB 10.0kV 14.6mm x300 SE(M)

UNB 15.0kV 15.0mm x4.50k SE(M)
5. SEM
Buck:
Early diagenetic phase in calcite laminae (pre-compaction & organic degradation)

Algal (?Pediastrum) or substrate coccoid bacteria?
Calcite platelets (? Calc green algae)
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Buck:
Early diagenetic phase in calcite laminae
(pre-compaction & organic degradation)

CFA:

\[ \text{Ca}_{10-a-b-c} \text{Na}_a \text{Mg}_b (\text{PO}_4)_{6-x} (\text{CO}_3)_{x-y-z} (\text{CO}_3,F)_y (\text{SO}_4)_z \text{F}_2 \]

where \(2c = x - y - a = \text{vacancies in the Ca site}\)

- F/P ratio is low, Ca/P is the expected apatite ratio of 1.67 \((r = 0.959)\)
- gradual reduction in Ca abundance correlates with increased Na (lattice substitution)
- reduction in S & P mitigated by >F content (counter charge imbalances in the lattice)
6. Models

If organic matter survives to burial, subsurface (bio-) geochemical degradation releases P into the pore waters.

-diffusion gradient = migration back to sed:water interface
6. Models

Anoxic interface = P returns to water column

Oxic interface = P adsorbed onto Fe/Mn oxyhydroxides
Most interpretations of P-rich black shales require (transient) oxic-anoxic transitions to bring P to supersaturation (with Ca, F, & S & REE) & precipitate CFA.

\[ \text{biogeochem release rate} > \text{Diffusion rate in sulfate reducing zone} \]
\[ = P \text{ saturation} \]
7. Summary

Phosphorus (& U, REE) anomalies occur in some upper Green River Fm. oil shale beds
- several anomalies with unique elemental proportions (possibly basinwide correlatable)

Elements combined in early diagenetic calcium fluorapatite
- in part fossilizing algae/substrate bacteria

Diagenetic conditions debatable
- oxic substrate not needed

Why not with ALL oil shales (e.g. 128.2 but not 131m)?
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Comments, Questions?