Mineralogical changes in Green River Formation oil shales following pyrolysis

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- Ronald Hill – now with Marathon Oil (APM shale)
This work is part of a laboratory study examining how different reaction conditions affect the composition of pyrolysis products for a variety of Green River oil shales.

Objectives include:

- Determine differences in oil & gas yields under different pyrolysis conditions
- Characterize shale oils generated by different pyrolysis methods
- Determine changes in shale residue mineralogy following pyrolysis
Green River Formation Mineralogy

Marlstones
Evaporites
Illitic shale
Etc.
Green River Formation samples

Two Mahogany zone samples (Piceance and Uinta Basins) and an illitic shale sample from the Garden Gulch Member (bottom R1)
Effects of retorting on oil shale mineralogy

Decomposition of carbonates and other minerals
Formation of new mineral phases
$\text{CO}_2$ release, effects on leachability, fracturing?

Other Issues
- Mineral effects on kerogen-bitumen-oil reactions
- Heavy oil retention and cracking (clays)

Fischer Assay

ASTM standard method for determining oil yield potential of oil shale

Rock is heated to 500°C at 12°C/min (40 min heat-up) and held for 40 min at atmospheric pressure

Oil, water and residual (spent) shale are collected

No gases are recovered (gas yield estimated as gas+loss)

Oil product yield and composition is comparable to surface retorting methods
In Situ Simulator

Pressure tested and purged with He (1000 psia) then evacuated $P_0 < 0.6$ psia

Preparation

Helium purged and evacuated $P_0 < 0.6$ psia

~20°C

Valves closed

<5°C

100-g oil shale

Electric heater $\Delta T/\Delta t = 3°C/min$

250-mL Parr reactor

500-mL Parr reactor

Coolant bath

USGS
**In Situ Simulator**

Pyrolysis

- Sample is heated to 360 °C and held 72 hours
- 420 < $P_0$ < 1275 psia
- $P_0$ < 0.6 psia

Valves closed

Oil vapor and Gas

**Diagram**

- Reactor pressure (psig)
- Pyrolysis time (hrs)
- APM
After the desired pyrolysis time has passed, the reactor is vented to the collector (complete in <1 min).
Both the reactor and collector are brought to room temperature (~24 hours) prior to recovery of spent shale and products.
Hydrous Pyrolysis

- Preparation:
  - Source Rock: 200 g
  - Water: 400 g
  - He (25 psia)
- Heat-up
- Pyrolysis: 360°C for 72 h
- Collection
  - Generated Gases
  - Expelled Oil
  - Spent Rock

Source: USGS
Results – *Pyrolysis*

**TOC = 19.3 wt%**

**Fischer Assay** has the highest oil yield. **Hydrous Pyrolysis** and **ISS** yields were ~70% and ~30% of **Fischer Assay**, respectively.

**In Situ Simulator** generated the lightest oil, and **Fischer Assay** produced the heaviest. Differences between shales were minimal.
Results – Pyrolysis

In the Piceance Basin samples, Hydrous Pyrolysis generated the most gas. All gas yields were approx. equal for the Uinta Basin Mahogany sample.
Results – XRD

Anvil Points Mahogany

ISS: Minor changes; dolomite shifts to calcite, some quartz loss, analcime generation

HP: Complete loss of dolomite & quartz; generation of smectite & calcite

FA: Similar changes to ISS; less dolomite-to-calcite conversion
**Results – XRD**

**Park Canyon Mahogany**

- **ISS**: Major carbonate changes; loss of quartz, gain in illite
- **HP**: Complete loss of dolomite, aragonite & most quartz; calcite & smectite formed
- **FA**: Loss of aragonite and some dolomite & quartz; increase in calcite
**Results – XRD**

**Garden Gulch Member**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>GGM Raw</th>
<th>GGM ISS</th>
<th>GGM HP</th>
<th>GGM FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite-ankerite</td>
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<tr>
<td>Calcite</td>
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<td>Aragonite</td>
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<td>Illite</td>
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<td>Quartz</td>
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<td>Albite</td>
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<tr>
<td>Feldspars</td>
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<tr>
<td>Analcime</td>
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<tr>
<td>Pyrrhotite</td>
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<tr>
<td>Smectite</td>
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</tr>
</tbody>
</table>

**ISS:** Some illite loss with other very minor changes

**HP:** Loss of dolomite & some illite; quartz unchanged; calcite, smectite & albite formed

**FA:** Changes similar to those observed in ISS (very minor)
Results

XRD Summary
Results – *FTIR*

- **Anvil Points Mine oil shale**
- **After ISS**
- **After HP**
- **After FA**

**Carbonate (C-O stretch)**

- **1430-1450 cm\(^{-1}\)**

**Silicates (Si-O stretch)**

- **900 - 1300 cm\(^{-1}\)**

**Narrowing due to conversion of dolomite to calcite**

**Loss of quartz**

**Dolomite 882 cm\(^{-1}\)**

- **Aliphatic carbon**
  - **2860 - 2960 cm\(^{-1}\)**

- **Illite 3625 cm\(^{-1}\)**

- **Smectite 3677 cm\(^{-1}\)**

- **3615 cm\(^{-1}\)**
Results – FTIR

- **Park Canyon oil shale**
- After ISS
- After HP
- After FA

Carbonate (C-O stretch) 1430-1450 cm⁻¹

Narrowing due to conversion of dolomite to calcite

Silicates (Si-O stretch) 900 - 1300 cm⁻¹

Loss of quartz

Ankerite 876 cm⁻¹

Normalised absorbance

Wavenumber (cm⁻¹)

- Smectite (saponite) 3677 & 3712 cm⁻¹
- Illite 3625 cm⁻¹
- Carbonate 2530 - 2550 cm⁻¹
- Aliphatic carbon 2860 - 2960 cm⁻¹
Results – *FTIR*

- **GGM Illitic oil shale**
- **After ISS**
- **After HP**
- **After FA**

**Normalized absorbance**

- **Aliphatic carbon**: 2860 - 2960 cm\(^{-1}\)
- **Illite**: 3625 cm\(^{-1}\)
- **Carbonate (C-O stretch)**: 1430-1450 cm\(^{-1}\)
- **Silicates (Si-O stretch)**: 900 - 1300 cm\(^{-1}\)
- **Dolomite**: 883 cm\(^{-1}\)
- **Some quartz loss indicated (not seen in XRD results)**
Mineral Reactions

“Conserved” species

Feldspars
(K,Na,Ca,NH₄)AlSi₃O₈
Overall, little change in feldspar content, though some species (buddingtonite) are decomposing

Albite
NaAlSi₃O₈
Albite content nearly constant in all experiments, except for increase following Hydrous Pyrolysis of Garden Gulch shale

Reactive minerals

Ankerite
Ca(Fe,Mg)(CO₃)₂
Aragonite
Ca(CO₃)
Dolomite
CaMg(CO₃)₂
Quartz
SiO₂

- Mineral reactivity varies with sample source and pyrolysis method
- Dolomites/ankerites completely converted to calcite and CO₂ in HP
- Quartz reactivity higher in marlstones
Mineral Reactions

Minerals formed

- Smectite
  \[ \text{Ca}_{0.25}(\text{Mg,Fe})_3(\text{Si,Al})_4\text{O}_{10} \text{(OH)}_2 \text{n[H}_2\text{O]} \]
- Calcite
  \[ \text{Ca(CO}_3) \]
- Illite
  \[ (\text{K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10} [(\text{OH})_2,(\text{H}_2\text{O})] \]
- Analcime
  \[ \text{NaAlSi}_2\text{O}_6 \text{[H}_2\text{O]} \]

- Smectite phase formed in all Hydrous Pyrolysis experiments
- Calcite re-precipitating after dissolution of other carbonates?
- Illite formed during pyrolysis of marlstones?
- Analcime formed during ISS and Fischer Assay of Anvil Points samples?
Smectite formation during Hydrous Pyrolysis

Ankerite

\[ 3 \text{Ca(Fe,Mg)(CO}_3\text{)}_2 + \text{NaAlSi}_2\text{O}_6 [\text{H}_2\text{O}] \rightarrow \text{Smectite (saponite)} + 5 \text{H}_2\text{O} \]

Analcime

\[ \text{NaAlSi}_2\text{O}_6 [\text{H}_2\text{O}] + 3 \text{Ca(Fe,Mg)(CO}_3\text{)}_2 \rightarrow \text{Calcite} + 6 \text{CO}_2 + 0.7 \text{Na}^+ \]

Issues

No detectable analcime in Park Canyon or Garden Gulch shales; quartz could be a source of Si and Al could be coming from illite, feldspars, etc.

Previous HP study showed conversion of smectite to illite when using an aqueous KCl solution (Roaldset et al., 1998, Clay Minerals v. 33, p. 147-158).

Bitumen impregnation of pore spaces could limit dissolution/re-precipitation reactions, but dolomite-to-calcite appears to be unaffected; could mineral reactions be occurring before kerogen-bitumen-oil conversion?

Subtle shifts in mineral composition that do not significantly affect the overall phase could make it difficult to understand some processes occurring – need more than bulk analysis.
How does water enter a bitumen-impregnated rock?

Prior to Petroleum Formation

~5% rock porosity
kerogen major OM phase
Dissolution/re-precipitation reactions possible
smectite-illite
opal-A-CT-Qtz

During Petroleum Formation

0% rock porosity
bitumen major OM phase
only solid transformation reactions possible
illite crystallinity
opal-CT crystallinity

Lewan, 1993
All shales were more susceptible to mineralogical changes under **Hydrous Pyrolysis** conditions
- Smectite formation in HP experiments consistent with results presented in 2010 by Palmer et al.

Under dry conditions, shifts were mostly minor, even under relatively high pressures in the **ISS**
- Exceptions include analcime formation in Piceance Mahogany and carbonate shifts in Uinta Mahogany

Some phases appear to be more easily degraded in particular samples
- Quartz unaffected in Garden Gulch Illitic shale, but significantly affected by pyrolysis in the Mahogany zone shales
- Could be due to differences in grain size, presence of other minerals, origin???