Dawsonite breakdown reactions during pyrolysis in Green River Formation oil shale

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Outline

• Saline Minerals in Green River Formation
• Dawsonite Breakdown
• Implications
Nahcolite resource outlines primary saline mineral zone

- Total in-place nahcolite (NaHCO$_3$) resource in thousands of tons per acre in the Parachute Creek and Garden Gulch Members of the Green River Formation, Piceance Basin, Rio Blanco County, Colorado
- Inferred extent of nahcolite depocenter outlined in red
# Evolutionary Stages Lake Uinta in the Piceance Creek Basin

<table>
<thead>
<tr>
<th>Stage</th>
<th>Zone w/mean max (gal/ton)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 Closing lake</td>
<td>R8, L7: Mean 18, Avg. Max 31.2</td>
<td>Progradation of siliciclastic sediments, closing of the lake</td>
</tr>
<tr>
<td>5 High lake</td>
<td>Mahogany: Mean 29.2, Avg. Max 66.1</td>
<td>Thick, laterally extensive rich oil shale beds</td>
</tr>
<tr>
<td>4 Rising lake</td>
<td>R6: Mean 24.7, Avg. Max 56</td>
<td>Thick beds, decrease of evaporites</td>
</tr>
<tr>
<td>3 Rapidly fluctuating lake</td>
<td>R5: Mean 20.9, Avg. Max 55.7, R4: Mean 31, Avg. Max 66.9</td>
<td>Highly cyclic units, thick evaporite beds</td>
</tr>
<tr>
<td>2 Transitional lake</td>
<td>R3: Mean 19.6, Avg. Max 38, R2: Mean 23.5, Avg. Max 40.8</td>
<td>High sand input</td>
</tr>
<tr>
<td>1 Fresh to brackish lake</td>
<td>R1: Mean 22.9, Avg. Max 53.7</td>
<td>Terrestrial organic material</td>
</tr>
</tbody>
</table>
Pyrolysis Reactions of Saline Mineral

• Nahcolite

\[ 2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

Nahcolite = Soda Ash + Water + Carbon Dioxide

\[ H_2O:CO_2 = 1:1 \]

• Dawsonite*

\[ 2 \text{NaAl(OH}_2\text{)CO}_3 = \text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 + 2 \text{H}_2\text{O} + \text{CO}_2 \]

Dawsonite = Soda Ash + Alumina + Water + Carbon Dioxide

\[ H_2O:CO_2 = 2:1 \]

* Reaction cited in Burnham, et al. 1983; patents to Shell, ExxonMobil
Well and Mine Locations
Fischer Assay data reveal saline mineral trend – USGS Colorado 1 Well

- Ternary Boundary
- Minerals
- Leached Zone
- Nahcolite Zone
- Illitic Zone
- Linear (Nahcolite Zone)
Fischer Assay data reveal saline mineral trend – USGS Colorado 1 Well
Simplified normative components from Fischer Assay

- Assumes loss part of gas+loss negligible
- Defines rich and lean zones
- Broadly indicates illitic oil shale and nahcolitic oil shale
- Nahcolite may be overestimated
- Relatively small fraction of carbonate reacts
CR-2 Mineralogy (Dean, Howell, Pitman, 1981)
USGS CR–2

- Minerals
- Illite Zone
- Dawsonite Zone
- Nahcolite Zone
- Nahcolite Trend

Dawsonite 1
Dawsonite 2
Nahcolite
Calcite
Gas + Loss
Water
Oil

COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT
USGS CR–2

Dawsonite 2
Nahcolite
Dawsonite 1

Ternary Boundary
Minerals
Upper Leached
Lower Leached
Illitic
Lower Dawsonitic
Upper Dawsonitic
Nahcolitic

Gas + Loss

Water

Residue
Additional Dawsonite Reaction

• Dawsonite breakdown*

\[
2 \text{NaAl(OH}_2\text{)CO}_3 = \text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 + 2 \text{H}_2\text{O} + \text{CO}_2
\]

Dawsonite = Soda ash + Alumina + Water + Carbon dioxide

\[H_2\text{O}:\text{CO}_2 = 2:1; \text{occurs above about 350°C}\]

• Soda Ash breakdown**

\[
\text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 = 2 \text{NaAlO}_2 + \text{CO}_2
\]

Soda ash + Alumina = Sodium aluminate + Carbon dioxide

\[\text{Cumulative } H_2\text{O}:\text{CO}_2 = 1:1; \text{above } \sim400°C \text{ (amorphous)}\]

* Reaction cited in Burnham, 1983; Shell, ExxonMobil patents

** Reaction cited by Huggins & Greene, 1973; implicit in Dyni patent
Dawsonite breakdown reactions

DA = Dawsonite - NaAl(OH)$_2$CO$_3$
AB = Albite - NaAlSi$_3$O$_8$
AN = Analcime - NaAlSi$_2$O$_6$$\cdot$H$_2$O
SA = Soda Ash - Na$_2$CO$_3$
AL = Alumina - Al$_2$O$_3$
QT = Quartz - SiO$_2$
NL = Sodium Aluminate - NaAlO$_2$
W = Water - H$_2$O
C = Carbon Dioxide - CO$_2$

$2\text{DA} = \text{nl} + \text{w} + \text{c}$

$\frac{2\text{DA} + \text{nl}}{\text{sa} + \text{al} + \text{w}}$

$\text{sa} + \text{al} = 2\text{nl} + \text{c}$

$\text{qt}$
Other potential reactions

• Topology dictated by phase relationships (Zen, 1966) and likely slopes of fluid phase reactions

• For oil shale, potential additional reactions involving silicates

\[
\text{NaAl(OH)}_2\text{CO}_3 + 3 \text{SiO}_2 = \text{NaAlSi}_3\text{O}_8 + \text{H}_2\text{O} + \text{CO}_2
\]

Dawsonite + Silica = Albite + Water + Carbon Dioxide

44.41g + 55.59g = 80.87g + 5.56g + 13.57g

• Additional reactions could also involve analcime
Dawsonite + quartz breakdown reactions

DA = Dawsonite - NaAl(OH)$_2$CO$_3$
AB = Albite - NaAlSi$_3$O$_8$
AN = Analcime - NaAlSi$_2$O$_6$•H$_2$O
SA = Soda Ash - Na$_2$CO$_3$
AL = Alumina - Al$_2$O$_3$
QT = Quartz - SiO$_2$
NL = Sodium Aluminate - NaAlO$_2$
W = Water - H$_2$O
C = Carbon Dioxide - CO$_2$

\[
\begin{align*}
DA + AB &= SA + CO + 3QT + W \\
2DA &= SA + AL + 2W + C \\
SA + AL + 6QT &= 2AB + C \\
SA + AL + 3QT &= AB + W + C \\
2DA + NL &= SA + AL + W \\
SA + AL &= 2NL + C
\end{align*}
\]
Do these reactions occur?

• May be kinetically precluded
• Appear to be involved in diagenesis in CR–2
CR–2 Mineralogy (Dean, Howell, Pitman, 1981)
Experiments on Oil Shale

- Sample from Horse Draw Mine (J. Dyni)
- Two types of retort:
  - Fischer Assay
  - In-Situ Simulator
- Characterized raw shale & products
  - XRD mineralogy
  - FTIR phase determination
  - Rock Eval
  - Gas composition
Experimental Results

All percentages adjusted to an original rock basis

- Raw Shale
- ISS Spent
- Fischer Spent

<table>
<thead>
<tr>
<th>Material</th>
<th>Raw Shale</th>
<th>ISS Spent</th>
<th>Fischer Spent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>35</td>
<td>37</td>
<td>25</td>
</tr>
<tr>
<td>Buddingtonite</td>
<td>20</td>
<td>22</td>
<td>15</td>
</tr>
<tr>
<td>Dawsonite</td>
<td>15</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>Illite</td>
<td>5</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Ankerite</td>
<td>2</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Gypsum</td>
<td>1</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sanidine</td>
<td>10</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>15</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Amorphous</td>
<td>30</td>
<td>32</td>
<td>25</td>
</tr>
</tbody>
</table>
Mineralogy Normalized to Residue

Mineral fraction only

- Raw Shale
- ISS Spent
- Fischer Spent

XRD-Rietveld wt %

Quartz, Buddingtonite, Dawsonite, Illite, Ankerite, Gypsum, Pyrite, Sandine, Pyrrhotite
FTIR Results

Normalized absorbance vs. wavenumber (cm\(^{-1}\))

- **Dawsonitic oil shale**
- **After ISS pyrolysis**
- **After Fischer Assay pyrolysis**

**Key Features**

- **Dawsonite peaks**
- **Silicates**
- **Dawsonite & other carbonates (Na-carbonate, ankerite)**
- **Aliphatic carbon**
# Yield and Rock Eval Data for Dawsonitic Oil Shale

<table>
<thead>
<tr>
<th></th>
<th>In Situ Simulator (ISS)</th>
<th>Fischer Assay (FA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil (mg/g-rock)</td>
<td>23.7</td>
<td>82.7</td>
</tr>
<tr>
<td>Gas (mg/g-rock)</td>
<td>28.9</td>
<td>37.0</td>
</tr>
<tr>
<td>Water (mg/g-rock)</td>
<td>0.0</td>
<td>43.9</td>
</tr>
<tr>
<td>Residue (mg/g-rock)</td>
<td>901.0</td>
<td>836.4</td>
</tr>
<tr>
<td>Oil Specific Gravity</td>
<td>0.782</td>
<td>0.915</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Raw Shale</th>
<th>ISS Spent</th>
<th>FA Spent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$ (mg-HC/g)</td>
<td>9.77</td>
<td>15.42</td>
<td>1.07</td>
</tr>
<tr>
<td>$S_2$ (mg-HC/g)</td>
<td>79.63</td>
<td>9.23</td>
<td>0.11</td>
</tr>
<tr>
<td>$S_3$ (mg-CO$_2$/g)</td>
<td>7.07</td>
<td>1.9</td>
<td>2.47</td>
</tr>
<tr>
<td>TOC (wt %)</td>
<td>9.89</td>
<td>5.35</td>
<td>3.5</td>
</tr>
</tbody>
</table>
ISS Gas Composition

• CO₂ represents 43 mol % (57 wt %)
• 100 g dawsonitic shale heated in ISS at 360 °C for 72 h generates ~1.8 g of CO₂
• Assuming
  – all dawsonite degraded (verified by FTIR and XRD)
  – degradation of each dawsonite “unit” releases one molecule of CO₂,
  – (based on 100 g sample, 5.5 wt % XRD data)
• 1.7 g of CO₂ generated by 5.5 g of dawsonite.
• Rock Eval S₃ indicates 700 mg of CO₂ would be generated by pyrolysis of 100 g of dawsonitic shale
  – S₃ does not represent total CO₂ potential of a sample; it is meant to be the organic–derived CO₂, released between 300–390 °C).
Conclusions

• Experimental results in FA and ISS suggest that quartz + dawsonite reaction does not take place
• Reasonable likelihood that reaction to sodium aluminate does occur
• Some increase in feldspar component also possible
• Dawsonite reaction to silicate minerals appears to occur in natural diagenetic systems
• Unclear under what in situ retorting conditions silicate reaction might occur
Implications of Alternative Dawsonite Breakdown Reaction

• Release of most CO$_2$ from dawsonite would add to carbon footprint of saline zone oil shale production
• Effect of release of CO$_2$ and H$_2$O near pyrolysis temperature range on pyrolysis products?
• Kinetic data needed to determine importance of silicate reactions for heat and mass balance
• Potential of sodium aluminate as a catalyst for organic reactions
• Does Al resource warrant concern about recovery in feldspars?
• Dawsonite as a mineral sequestrant for CO$_2$
BACKUP SLIDES
Classification for Mudrocks
(75 solid vol % ≤ 62 μm)
Classification for Mudrocks
(75 solid vol % ≤ 62 μm)
Classification for Mudrocks
(75 solid vol % ≤ 62 μm)
Additional CO$_2$ release from Nahcolite

![Graph showing CO$_2$ release and production quality](image)

- Diamond markers: Nahcolite 19%
- Square markers: Nahcolite 0.8%

Production Quality (FA*FA%*Power plant eff.)

CO$_2$ (tons per barrel)
Water release from nahcolitic oil shale

![Graph showing water release vs. Kerogen/Nahcolite ratio]
Richness controls CO$_2$ release
USGS CR-1 Well

- Dawsonite 1
- Dawsonite 2
- Nahcolite

Minerals
- Water
- Gas

Ternary Boundary
- 0-1422 ft
- 1729-2129.8 ft
- 2129.6-2536 ft
- Minerals
Shale and Mudstone Mineralogy

- **Carbonate**
  - Calcareous/dolomitic mudstone
  - Argillaceous marlstone
  - Siliceous marlstone

- **Quartz + Feldspar**
  - Q+F=Clay
  - Carbonate/Clastic

- **Clay Minerals**
  - Clay Minerals
  - Average Shale (1975)
  - Bakken
  - Barnett
  - U. Green River
  - L. Green River
  - Chinese Oil Shale
  - Thailand Oil Shale
  - Polish Gas Shale
  - Duvernay
  - Muskwa
  - Besa R. Lower black shale
  - Besa R. Upper black shale
  - Fort Simpson
### Relationship of Climate and Lake Stratigraphy

<table>
<thead>
<tr>
<th>Lake Level</th>
<th>O.S. Zone</th>
<th>Climate, Vegetation</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Stable</td>
<td>Wet, high runoff</td>
<td>Laminated oil shale</td>
</tr>
<tr>
<td>Low</td>
<td>Unstable</td>
<td>High vegetated source: algal, and terrestrial input</td>
<td>Shore carbonates (stromatolites, tufa)</td>
</tr>
<tr>
<td>Low</td>
<td>Stable</td>
<td>Dry, low runoff</td>
<td>Oil shale breccias, disturbed o.s deposits</td>
</tr>
<tr>
<td>Low</td>
<td>Unstable</td>
<td>Low vegetated source: algal input</td>
<td>Channelized sandstones</td>
</tr>
<tr>
<td>Low</td>
<td>Stable</td>
<td></td>
<td>Turbidites, hyperpycnites</td>
</tr>
<tr>
<td>Low</td>
<td>Unstable</td>
<td></td>
<td>Laminated o.s</td>
</tr>
<tr>
<td>Low</td>
<td>Stable</td>
<td></td>
<td>Aeolian siltstones</td>
</tr>
<tr>
<td>Low</td>
<td>Unstable</td>
<td></td>
<td>Evaporites</td>
</tr>
</tbody>
</table>

**Legend:**
- SB: Stable Baseline
- H: High
- R: Rising
- L: Low

*Note: The figure illustrates how changes in lake level and climate affect the deposition of sediments. High vegetation and wet conditions lead to laminated oil shale, while dry conditions result in evaporites.*
Nahcolite breakdown (after Templeton, 1978)

- Reactions conducted at constant Vg/Vs
- Calculated for Vg/Vs = 0
- U. S. Bureau of Mines/AEC Colorado #1 well used as representative
- At lithostatic load of saline zone, reaction occurs at ~200°C
- Substantially below pyrolysis temperature
Volume change for kerogen and nahcolite

Kerogen

<table>
<thead>
<tr>
<th></th>
<th>Volume (ft³)</th>
<th>before</th>
<th>after</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC Liquid</td>
<td>15.3</td>
<td>26.1</td>
<td></td>
</tr>
<tr>
<td>HC Vapor</td>
<td>6.6</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>Coke</td>
<td>8.1</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Kerogen</td>
<td>7.2</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>Mineral</td>
<td>2.9</td>
<td>6.6</td>
<td></td>
</tr>
</tbody>
</table>

Nahcolite

<table>
<thead>
<tr>
<th></th>
<th>Volume (ft³)</th>
<th>before</th>
<th>after</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>17.4</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>8.1</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>Natrite</td>
<td>8.1</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Nahcolite</td>
<td>6.3</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Kerogen</td>
<td>6.3</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>Mineral</td>
<td>6.3</td>
<td>6.3</td>
<td></td>
</tr>
</tbody>
</table>

225°C
150 bar
~2160 feet
Will it fracture the rock?

\[ 2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

$2 \times 81.4 \text{g/mol}$ \hspace{1cm} $106 \text{g/mol}$ \hspace{1cm} $18 \text{g/mol}$ \hspace{1cm} $44 \text{g/mol}$

$2.173 \text{g/cc}$ \hspace{1cm} $2.54 \text{g/cc}$

$2 \times 38.66 \text{cc/mol}$ \hspace{1cm} $41.73 \text{cc/mol}$

$\Delta \text{Volume (solids)} = -35.59 \text{cc/mol} = 44\%$

Fluid density in void $= 18 + 44 \text{ g/35.594 cc} = 1.742 \text{ g/cc}$

Density of $\text{CO}_2$ alone $= 44\text{g/35.594cc} = 1.236 \text{ g/cc}$

Density of water alone $= 18/35.594 = 0.506 \text{ g/cc}$
Can water alone fracture the rock?

- Large volume change to steam
- Occurs at higher T
- Upper zone generally leached
- Increased porosity may accommodate volume increase
- Will activity of water affect pyrolysis?
Sodium Carbonate Minerals in Colorado, Utah, and Wyoming

- World’s largest sodium carbonate deposit – Wilkins Peak Member of the GRF, Green River Basin, SW Wyoming as trona (Na₃(CO₃)(HCO₃) · 2H₂O)
- Second largest sodium carbonate deposit – Parachute Creek Member of the GRF, Piceance Basin, NW Colorado as Nahcolite (NaHCO₃)
- Minor bedded sodium carbonate deposits in the GRF Uinta Basin contains near Duchesne, Utah
- Dawsonite is widespread in the lower part of the saline zone of the Piceance Basin, comprising up to ~25% of the rock