Deposition and Diagenesis of Basin-Center Evaporites, Green River Formation

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How can study of evaporite deposition and diagenesis in the Green River Formation help us further understand the accumulation, preservation, and development of oil shale?
1. Paleoenvironments in which evaporites and oil shales were deposited.
3. Hydrocarbon droplets in fluid inclusions.
4. Sodium carbonates and Eocene $pCO_2$
5. Mineralogical puzzles?
Lacustrine Deposits of the Eocene Green River Formation

GRB: Green River Basin
WB: Washakie Basin
PCB: Piceance Creek Basin
UB: Uinta Basin

Minerals:
Nahcolite = $\text{NaHCO}_3$
Trona = $\text{NaHCO}_3\cdot\text{Na}_2\text{CO}_3\cdot2\text{H}_2\text{O}$

Largest Reserves in World
From Dyni, 1998
Stratigraphic section, Green River Formation, Piceance Creek basin.

Oil Shale resources: predominantly saline lake deposits.

from Dyni, 2006.

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from Dyni, 2006.
Green River Formation, Piceance Creek Basin, Colorado

• Fine laminae with nahcolite, halite, dolomite, dawsonite \([\text{NaAl(OH)}_2\text{CO}_3]\), and organic matter: detrital sediment and chemical precipitates

• Vertical, bottom growth of halite with no dissolution of saline minerals

• Density stratified saline lake-preservation of organic matter

$10^7$-$10^8$ cells/ml
2. Fluid inclusion Microthermometry:

Primary fluid inclusions trapped in halite and other saline minerals:

- temperatures of paleolakes
- temperatures of diagenetic mineral formation
Fluid Inclusion Microthermometry:
Single-phase brine trapped during crystal growth (left).
Cool in freezer so vapor bubbles nucleate (right).
Heat sample slowly to temperature at which vapor bubble disappears—“HOMOGENIZATION TEMPERATURE” (temperature of brine in which halite crystal grew).
Death Valley
Paleolake Temperatures

Lowenstein et al. 1998
3. Hydrocarbon droplets in fluid inclusions. Some primary fluid inclusions in halite from the Piceance Creek basin that crystallized at the brine bottom contain liquid hydrocarbons.
Linear arrays of negative cubic fluid inclusions

Bottom-growth halite and chemical-detrital mud layers

Cubic fluid inclusion with brine + liquid hydrocarbon droplets on needle of nahcolite (?)
Primary fluid inclusions in halite contain liquid hydrocarbons and nahcolite, both trapped during crystal growth at brine bottom. What does this mean? Hydrocarbon seeps on lake floor?
4. Sodium carbonates and Eocene pCO₂

Sodium carbonate mineral equilibria and partial pressure of CO₂ in the system NaCl-NaHCO₃-Na₂CO₃-H₂O

Total pressure 1 atm, Solution + minerals in equilibrium

Minerals:
Nahcolite = NaHCO₃
Trona = NaHCO₃•Na₂CO₃•2H₂O
Natron = Na₂CO₃•10H₂O

Lowenstein and Demicco, 2006; modified from Eugster, 1966
Modern Lake Magadi, Kenya: Trona

Dean and Fouch, 1983
Owens Lake, California: Trona, less than 100 years old

Trona + Halite + Mud
Green River Formation: Precipitation of Nahcolite and Halite cumulates at the air-water interface, in equilibrium with atmospheric CO$_2$. 
Conclusions:

Crystallization of nahcolite and halite from waters in contact with the atmosphere establishes that early Eocene $p\text{CO}_2 > 1125$ parts per million by volume.
5. Mineralogical Problem: trona and nahcolite occur in deposits of the same age!

(1) During deposition, GRB trona may have formed at higher temperatures than the PCB nahcolite.
(2) Green River trona may have formed from precursor phase (nahcolite?) during diagenesis at elevated temperatures.
Different brine chemistries, may have favored precipitation of trona in the Green River basin. 

\[ 2\text{NaHCO}_3\text{(nahc)} + 2\text{H}_2\text{O} + \text{Na}^+ \leftrightarrow \text{NaHCO}_3\cdot\text{Na}_2\text{CO}_3\cdot2\text{H}_2\text{O (tr)} + \text{H}^+ \]

indicates that trona forms in preference to nahcolite at high activity of \( \alpha_{\text{Na}^+} \) and high pH.
(4) High $p\text{CO}_2$ needed to form nahcolite may have been produced in lake waters and bottom sediments by organic processes operating in the Piceance Creek saline lake system.
1. Saline lake paleoenvironments in which evaporites and oil shales accumulated.

2. Fluid inclusions: temperatures of paleolakes and diagenesis

3. Hydrocarbon droplets in fluid inclusions

4. Sodium carbonates and Eocene CO$_2$

5. Mineralogical puzzles?

How is this useful for development of oil shale?