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## Saline Minerals in the Green River Formation, Green River and Washakie Basins, Wyoming

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### *Abstract*

The saline minerals of the Green River Formation consist of Ca, Na, and Mg carbonates and halides that were deposited during the dryer, evaporative phases of Eocene Lake Gosiute's history when the large lake may have dried to several smaller lakes. These minerals have continued to generate interest because of the large economic potential they represent. In Wyoming, the bedded trona deposits are recognized as the world's largest known resource of mineral sodium carbonate. To correlate stratigraphy and mineralogy, a series of ten core holes was evaluated by systematic X-ray diffraction (XRD). These data were used to delineate the distribution of the primary saline minerals trona, shortite, nahcolite, and northupite. Loughlinite, though not technically a carbonate salt, was included in this study because of the mineral's strong association and related genesis with other salts. Minor saline mineral phases identified by XRD, but generally only in small or trace amounts, included: halite, gaylussite, pirssonite, and wegscheiderite. Stratigraphic distribution, mineralogy, lithology, and statistical correlation were used to delineate the vertical and lateral extent of the saline minerals and help interpret their geochemical genesis.

### *Introduction and Background*

The lacustrine sediments of the Green River Formation in Colorado, Wyoming, and Utah have been the object of intense study for more than a hundred years. The Green River Formation is characterized by a unique assemblage of minerals, some of which have been found nowhere else (Milton, 1981). Much has been published concerning these lacustrine sediments. The unique assortment of authigenic and diagenetic minerals occurring in the formation has been described by many authors; Culbertson (1961) and more recently Roelher (1993) described the stratigraphy of Wyoming's Green River Formation, pointing out that the saline minerals occurred primarily in the Wilkins Peak Member and were absent from the oil shale of the underlying Tipton Member and the overlying Laney Member.

In Wyoming, the Green River Formation was deposited during a four million year interval during the Eocene in Lake Gosiute, which occupied parts of the present-day Green River, Washakie, Sand Wash, and

Great Divide Basins, covering an area of approximately 16,000 mi<sup>2</sup> (43,500 km<sup>2</sup>) in southwestern Wyoming and adjoining parts of Utah and Colorado. During its life, the lake passed through three major stages, each of which corresponds to a member of the formation; from oldest to youngest, these are:

1. The Tipton Member which consists of oil shale and scattered dolomitic mudstones, deposited over about a million years when the waters of Lake Gosiute were fresh.
2. The Wilkins Peak Member which consists of oil shale, marlstone, limestone, and evaporite minerals with beds of sandstone, siltstone, volcanic tuffs, and mudstones, deposited over about a million years when the climate became more arid and evaporation exceeded the supply of water. This climate resulted in the deposition of evaporitic and saline minerals.
3. The Laney Member which consists of oil shale, marlstone, fine-grained sandstone, and minor beds of limestone and altered tuffs, deposited over about 2

million years. It represents the third and longest stage when Lake Gosiute achieved its greatest expansion and the lake transitioned from a hydrologically closed basin, with hypersaline lakes and playas, returning to a fresh water, hydrologically open basin (Carroll and Bohacs, 1999).

Volcanic tuffs have been used by Rhodes et al. (2002) to date the Green River sequence to approximately 52 - 48 Ma. Robb and Smith (1976) demonstrated that the lacustrine sediments of the Green River Formation could be correlated with respect to stratigraphy and mineral facies over large geographic areas due to the unique depositional environment that created the sediments. Long periods of relatively steady environmental conditions created mineral suites that directly reflect the original depositional environment and subsequent diagenetic alterations.

### Methods

**Sample Selection:** Samples for this study were collected from 10 core holes located in the Green River and Washakie basins of Wyoming. Samples from core hole sources were used exclusively in order to increase stratigraphic accuracy, achieve continuous sample distribution, and minimize the effects of surface weathering. Core hole

sample sources were selected on the basis of geographic location, stratigraphic representation of the formation, and availability. Samples were selected on appropriate intervals to fully illustrate the lithologic and mineralogic variation of the section. Figure 1 illustrates the study area and location of core holes. Detailed location information about core holes used in this study is presented in Table 1.

**Experimental Procedures:** Mineralogical characterization of the samples was performed by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Sediments of the Green River Formation are generally too fine-grained to be studied effectively by standard optical techniques. To more completely investigate these fine-grained sediments, an Amray 1810 Scanning Electron Microscope (SEM) equipped with an energy dispersive X-Ray analyzer (EDX) was used to investigate selected samples.

Data on oil yield determined by Fischer Assay were acquired at the Laramie Energy Technology Center (formerly operated by U. S. Bureau of Mines and later by the U. S. Department of Energy) and were obtained from the data archives. Both the X-ray diffraction measurements and the Fischer assays were completed on samples selected to represent the cores continuously. Selection of the samples for organic content and mineral surveys was based on visible lithologic variations so that each sample was as uniform as possible.

### Genesis of Saline Minerals

The Green River Formation contains a vast array of saline minerals that includes: shortite  $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ , northupite  $\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}$ , pirssonite  $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ , gaylusite  $\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ , nahcolite  $\text{NaHCO}_3$ , thermonatronite  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , wegscheiderite

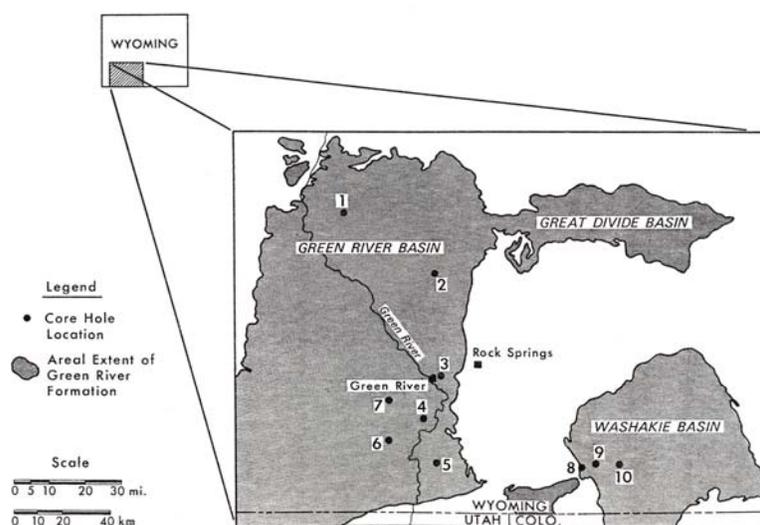


Figure 1: Green River Formation and location of sample sources.

Table 1. Detailed location information about core holes used in this study.

<i>Map</i>	<i>Name</i>	<i>Location</i>	<i>County, State</i>
1	U.S. Department of Energy/Laramie Energy Technology Center Wyoming core hole No. 14	SE1/4 SW1/4 NW1/4 of sec.33, T26N, R110W	Sweetwater County, WY
2	U.S. Bureau of Mines Wyoming core hole No. 1	NW1/4 SW1/4 NW1/4 of sec.30, T23N, R107W	Sweetwater County, WY
3	U.S. Energy Research and Development Administration/Laramie Energy Research Center and Rocky Mountain Energy Company White Mountain core hole No. 1	SW1/4 NE1/4 SW1/4 of sec. 7, T18N, R107W	Sweetwater County, WY
4	U.S. Energy Research and Development Administration/Laramie Energy Research Center Blacks Fork core hole No. 1	SE1/4 NE1/4 of sec. 24, T16N, R108W	Sweetwater County, WY.
5	U.S. Department of Energy/Laramie Energy Technology Center Currant Creek Ridge core hole No. 1	SE1/4 NW1/4 of sec. 14, T14N, R107W	Sweetwater County, WY
6	Union Pacific Railroad Company El Paso core hole No. 44-3	C SE1/4 SE1/4 of sec. 3, T15N, R109W	Sweetwater County, WY
7	Union Pacific Railroad Company Blacks Fork core hole No. 41-23	NE1/4 NE1/4 of sec. 23, T17N, R109W	Sweetwater County, WY
8	U.S. Bureau of Mines Washakie Basin core hole No. 1A	NW1/4 SW1/4 of sec. 17, T14N, R98W	Sweetwater County, WY
9	U.S. Bureau of Mines Washakie Basin core hole No. 1	SW1/4 SW1/4 SW1/4 of sec. 24, T14N, R100W	Sweetwater County, WY
10	U.S. Bureau of Mines Washakie Basin core hole No. 2	SW1/4 SW1/4 of sec. 6, T14N, R98W	Sweetwater County, WY

Na<sub>5</sub>(CO<sub>3</sub>)(HCO<sub>3</sub>), bradleyite  
 Na<sub>3</sub>Mg(PO<sub>4</sub>)(CO<sub>3</sub>), natron Na<sub>2</sub>CO<sub>3</sub> · 10H<sub>2</sub>O,  
 and tychite Na<sub>6</sub>Mg<sub>2</sub>(CO<sub>3</sub>)<sub>4</sub>(SO<sub>4</sub>), as well as  
 the associated silicate loughlinite  
 Na<sub>2</sub>Mg<sub>3</sub>Si<sub>6</sub>O<sub>16</sub> · 8H<sub>2</sub>O.

Lake Gosiute underwent numerous wet periods alternating with episodes of a nearly complete drying up of the lake. Culbertson (1961) counted at least 42 beds of trona, each of which could be interpreted as a "drying up" of the lake.

Eugster and Hardie (1975) found partings of dolomite and mudstone associated with nearly all trona beds. These minerals formed from either direct precipitation of Na-rich waters or from brines trapped within the sediments. Nahcolite formed when Na<sup>+</sup> from granite-derived feldspar-rich detrital sediments, produced Na<sub>2</sub>CO<sub>3</sub> in solution at high pH and high P<sub>CO2</sub>. Sodium

carbonate remained until the pH dropped and HCO<sup>-3</sup> increased, crystallizing nahcolite. The formation of nahcolite in this manner precludes an evaporitic origin (Smith, 1974).

Trona formed as (1) individual crystals in the sediments; or (2) as a thick monomineralogic beds that precipitated directly from the lake waters as it became supersaturated as a result of evaporation (Fahey, 1962).

Shortite can form by direct precipitation, when the temperature of the sediments reached approximately 90° C (Eugster and Smith, 1965). Northupite formed when a brine containing NaCl came in contact with shortite (Bradley and Eugster, 1969). Loughlinite, a Na-phyllosilicate form is associated in the same stratigraphic interval as the Na-salts.

Bradley and Eugster (1969) proposed two reactions for the formation of loughlinite: the first, when silica-bearing solutions came in contact with trona and dolomite; and the second, from shortite, forming when loughlinite crystallized below the sediment water interface, as shortite came in contact with trapped brines which were rich in silica, bicarbonate, and  $Mg^{+2}$  released from the organic material. Figure 2 shows the U.S. Energy Research and Development Administration/Laramie Energy Research Center Black's Fork core hole No. 1 with the lithology, formational contacts, oil yield, and saline mineral XRD peak heights indicated.

### Distribution of Saline Minerals

Halite, gaylussite, pirssonite, and wegscheiderite were identified in only rare occurrences in the Green River Basin; therefore, no attempt was made to graphically illustrate their distribution.

**Shortite:** Shortite occurred exclusively in the Wilkins Peak Member and was nearly continuous throughout the member. Shortite was detected in seven core holes in the Green River and Washakie basins and was principally concentrated in the Green River Basin, but it was also detected in the Washakie Basin at the very base of the Wilkins Peak Member and in three samples from USBM Washakie Basin No. 1. Shortite was most concentrated in the

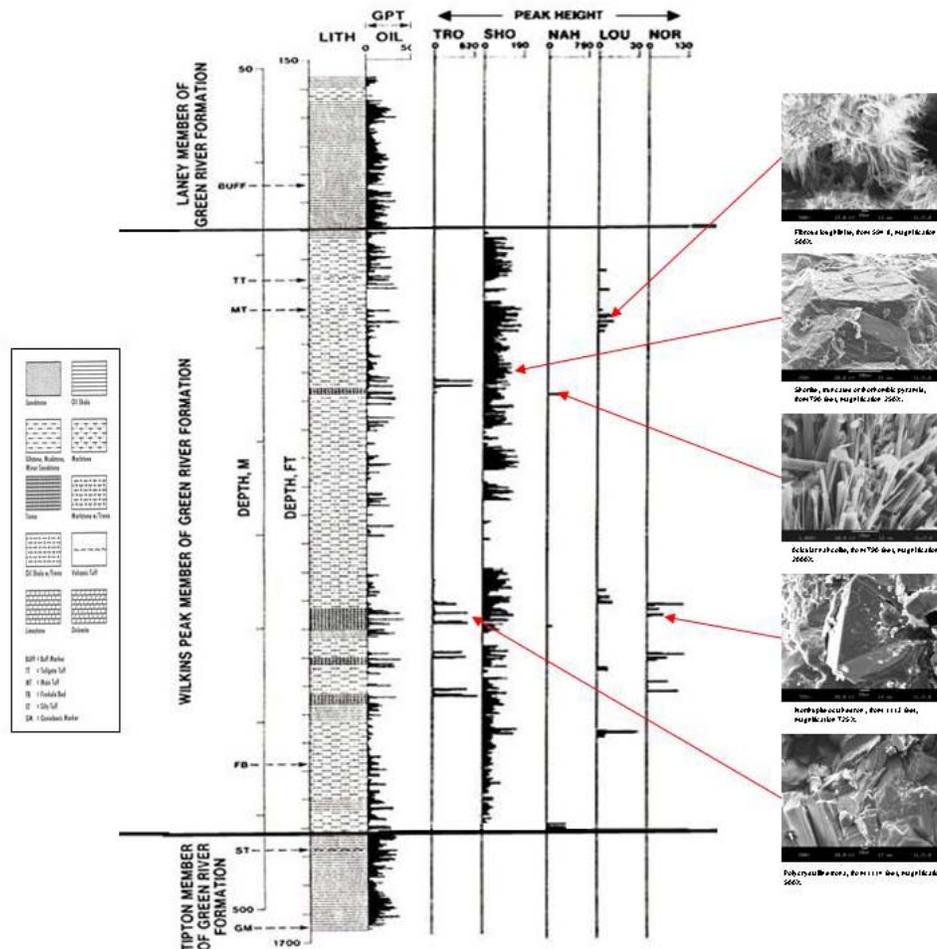


Figure 2: U.S. Energy Research and Development Administration/Laramie Energy Research Center Blacks Fork core hole No. 1 with the lithology, formational contacts, oil yield, and saline mineral XRD peak heights indicated. SEM photomicrographs of selected minerals are shown with arrows indicating sample location.

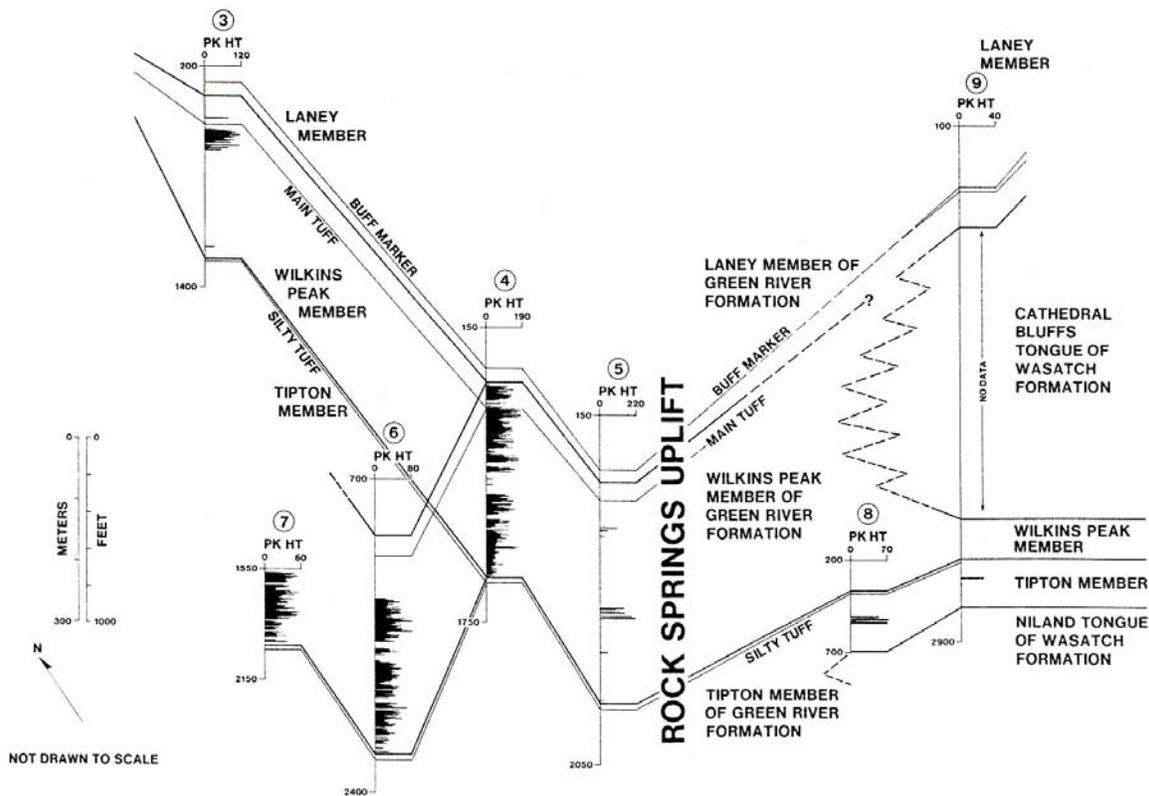


Figure 3: Distribution of shortite.

southern portion of the Green River Basin. The mineral was detected in ERDA Blacks Fork No. 1, UP El Paso No. 44-3, UP Blacks Fork No. 41-23, and in the DOE Currant Creek Ridge No. 1. Figure 3 illustrates the distribution of shortite.

*Trona:* Trona, an important economic mineral, is an indicator of the geochemical conditions. The intervals containing trona did not generally contain other saline minerals. Trona was abundant in the ERDA Blacks Fork No. 1, the UP El Paso No. 44-3 and the UP Blacks Fork No. 41-23 core holes. Only a single occurrence of trona was detected in the DOE Currant Creek Ridge No. 1 core hole, and trona was not detected in the Washakie Basin. Figure 4 illustrates the distribution of trona.

*Nahcolite:* Nahcolite is not considered a major mineral phase in the sediments of the Green River Formation in Wyoming. Lake Gosiute has been considered too saline for the formation of nahcolite and

rather the conditions were considered to favor the formation of shortite and trona. Nahcolite was detected in four core holes in the Green River Basin and in two core holes in the Washakie Basin. Nahcolite may have formed at an early stage of saline mineral formation, preceding the precipitation of thick-bedded trona deposits. As the geochemical conditions became increasingly more saline, shortite and trona were favored over nahcolite. The occurrence of nahcolite just above the Tipton-Wilkins Peak boundary indicates less saline conditions, possibly caused by seasonal influxes of fresh water or slight climatic changes. Figure 5 illustrates the distribution of nahcolite.

*Loughlinite:* Loughlinite formed in the Wilkins Peak Member when silica-bearing solutions came in contact with sodium carbonate brines. Loughlinite was detected in four core holes in the Green River Basin, ERDA White Mountain No. 1, ERDA Blacks

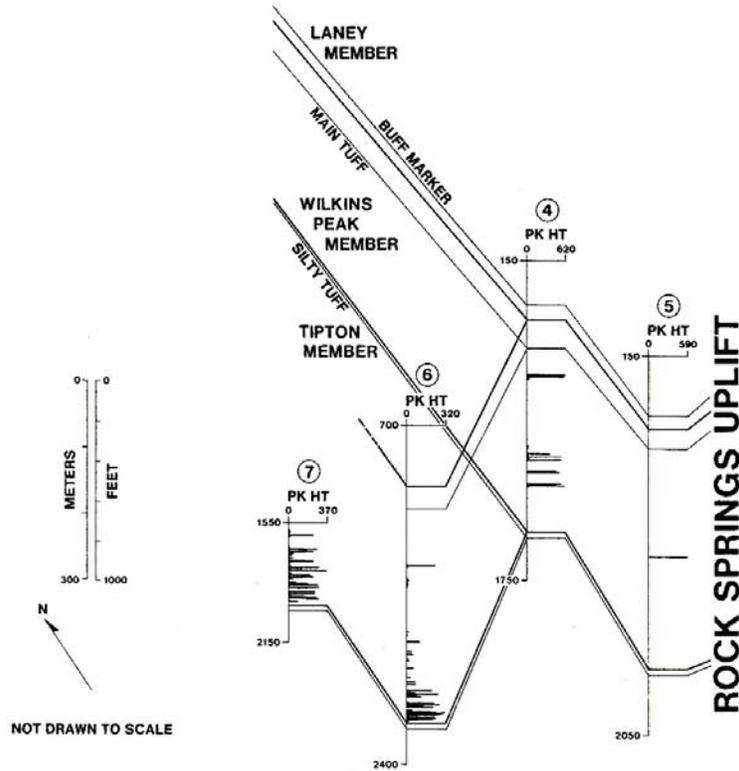


Figure 4. Distribution of trona.

Fork No. 1, UP El Paso No. 44-3, UP Blacks Fork No. 41-23 and one core hole in the Washakie Basin, USBM Washakie Basin No.

1. The identification of loughlinite in the ERDA White Mountain No. 1 and the USBM Washakie Basin No. 1 was significant be-

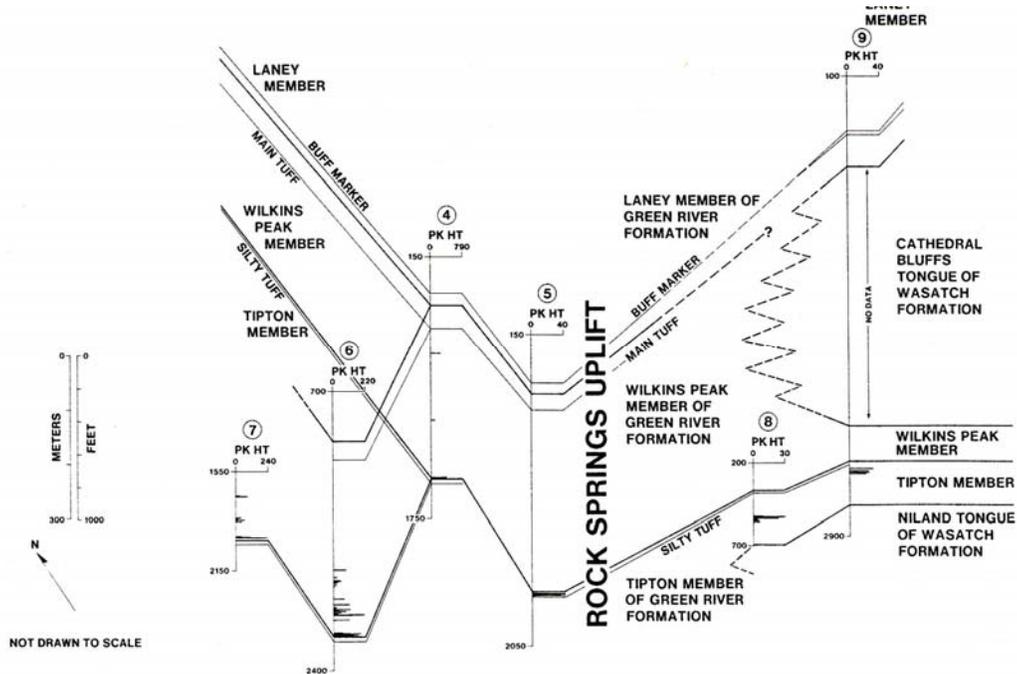


Figure 5. Distribution of nahcolite.

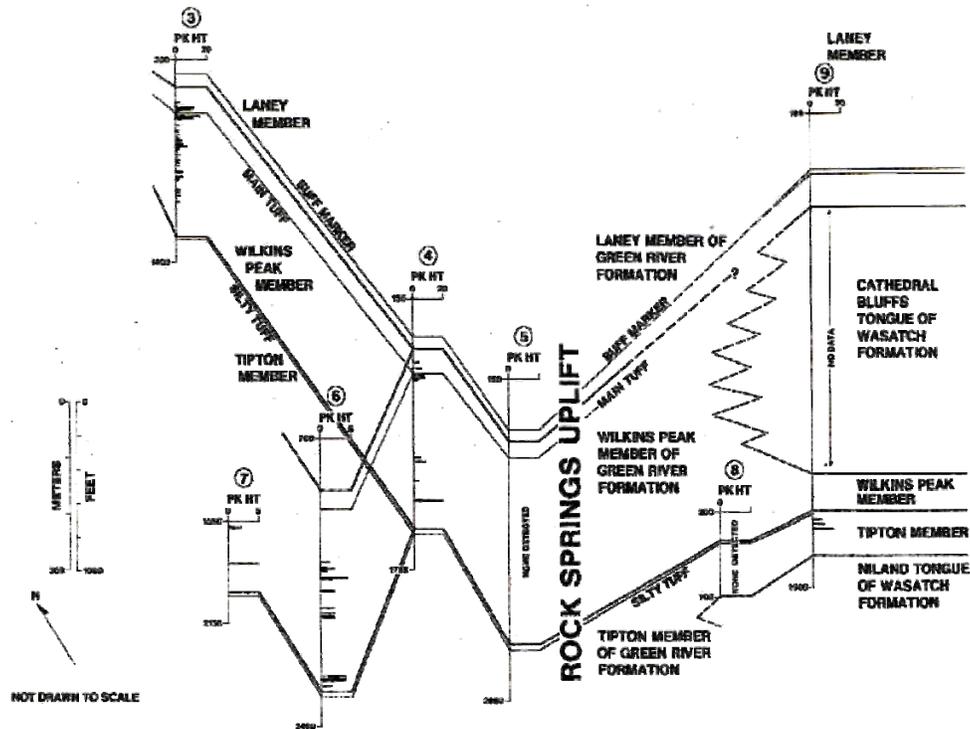


Figure 6. Distribution of loughlinite.

cause no trona was identified in either of these core holes. If the genesis of loughlinite were related to the presence of trona, then conditions of trona deposition may have extended further than previously recorded and the trona deposited has subsequently been altered or removed by solution. Figure 6 illustrates the distribution of loughlinite.

**Northupite:** Northupite was detected in the Wilkins Peak Member and is limited to the saline zones that in which halite is generally absent. The extremely strong correlation of northupite and trona supports the genesis as resulting from interaction of sodium carbonate brines with halite. The distribution of northupite was limited to three core holes in the study area: ERDA Blacks Fork No. 1, UP El Paso No. 44-3, and UP Blacks Fork No. 41-23. Of these core holes, only the UP El Paso No.44-3 displayed any quantity of northupite. Figure 7 illustrates the distribution of northupite.

### Conclusions

The formation of saline minerals in the Green River Formation of Wyoming can be summarized by the criteria needed for the genesis of these sodium/calcium minerals:

1. A source of necessary Na and Ca cations from the erosion of feldspar-rich granitoid rocks
2. Carbonate and bicarbonate anions provided by the fermentation of the rich organic matter in the lake bottom and waters and their subsequent contribution to the rise in alkalinity of the lake
3. A warm, arid climate where evaporation exceeded precipitation or recharge, providing a triggering mechanism for the precipitation of the saline minerals
4. Stable climatic and tectonic conditions, that allowed Lake Gosiute to remain in relative stasis

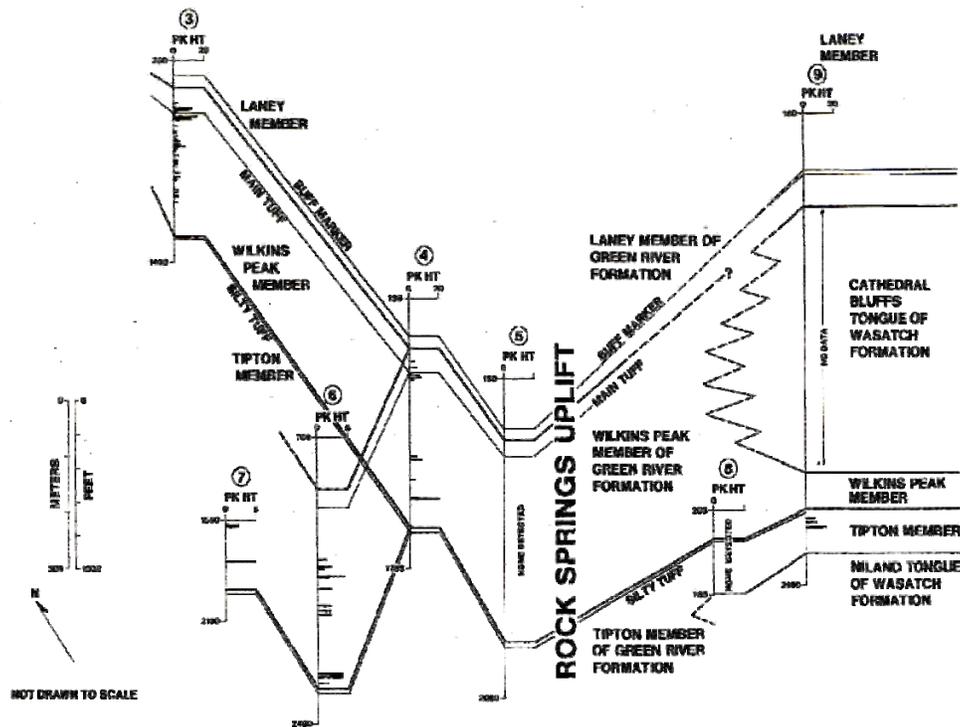


Figure 7: Distribution of northupite.

- Time - the Wilkins Peak Member persisted for approximately a million years, allowing enormous quantities of saline minerals to be precipitated.

Minor changes in these conditions are reflected by the specific mineral species, as well as distribution of the mineral geographically.

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