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## ABSTRACT

The discovery of exquisitely preserved filamentous bacteria from the Green River Formation, Green River Basin, Wyoming suggests a relationship between bacteria and the formation of the iron carbonate mineral, siderite ( $\text{FeCO}_3$ ). Comparative mineralogical studies of the Green River Formation, have suggested a previously undefined controlling mechanism for siderite precipitation/distribution. Most abundant at the of the Tipton/Wilkins Peak boundary, siderite has been characterized geochemically as part of a drying and concentrating episode of Lake Gosiute. This period in the lake's history would have had a high potential for increased alkalinity and available ionic iron leached from volcanoclastic sources. Siderite is known to precipitate from saturated solutions which are in equilibrium with  $\text{CO}_2$  gas or contain a fixed amount of carbonate ions. Another possibility for siderite formation that has been suggested is a bacterial origin involving the reduction of iron in anaerobic sediments. Certain modern filamentous bacteria for example, *Liptothrix* and *Crenothrix*, are characterized by flocculent masses of hydrated ferric hydroxide which is collected on a bacterial sheath. As the bacteria shed their sheath and grow a new one, they leave behind an iron-rich bacterial framework which might serve as a center for siderite nucleation. New Scanning Electron Microscopic (SEM) observations have identified Eocene Age fossilized bacteriamorphs from the Tipton/Wilkins Peak boundary which bear an uncanny resemblance to their modern counterparts. These data seem to suggest validation for a bacterial genesis of siderite.

## 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 known nowhere else. 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; 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 as 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  $\text{mi}^2$  (43,500  $\text{km}^2$ ) 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, are: the Tipton Member which consists of oil shale and scattered dolomitic mudstones, lasted about a million years and was deposited when the waters of Lake Gosiute were fresh; the Wilkins Peak Member which consists of oil shale, marlstone, limestone, and evaporite minerals with beds of sandstone, siltstone, volcanic tuffs, and mudstones, lasted about a million years and was deposited when the climate became more arid and evaporation exceeded the supply of water which resulted in the deposition of evaporitic and saline minerals; and the Laney Member which consists of oil shale, marlstone, fine-grained sandstone, and minor beds of limestone and altered tuffs, lasted about 2 million years and 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, and returned 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 mya. Figure 1 is a view of the sediments of the Green River Formation, along the shores of Flaming Gorge Reservoir, as they appear today.



Figure 1. The Green River Formation, as it appears today, along Flaming Gorge Reservoir.

## METHODS AND SAMPLE SOURCE

Samples for this work came from the U. S. Energy Research and Development Administration/Laramie Energy Research Center, Black's Fork Core Hole No.1, located in SE1/4 of the NE1/4 of sec. 24, T16 N, R 108 W, Sweetwater County, Wyoming drilled in 1976. Individual samples for study were selected based on lithology, mineralogy, and availability. The Black's Fork Core Hole No. 1 was cored from a depth of 181.0 to bottom of hole at 1676.6 feet with the bore hole terminating in the Wasatch Formation. Figure 2 illustrates the areal extent of the Green River Formation in Wyoming and geographic location of the Blacks Fork Core Hole from which the samples of sediment containing the fossil bacteriamorphs were obtained.

The original lithologic description was prepared at the Laramie Energy Technology Center (LETC) by L. G. Trudell in 1979. Detailed mineralogical characterization of samples was performed by X-ray diffraction (XRD) using peak heights, to approximate mineral abundance relationships.

Sediments of the Green River Formation, except for clastic units and some tuffaceous horizons, are too fine-grained to be studied effectively by standard optical techniques. The average particle size of Green River Formation sediments to be in the 5 micrometer particle size. Since more than 90% of bacteria fall within the 0.5 to 2 micrometer size range, Scanning Electron Microscopy (SEM) was utilized as being the best available method to investigate the sediments. Of note, the original observation of bacteriamorphs in Green River Formation sediments occurred completely by accident as the author was examining core samples for mineral relationships unrelated to bacteria morphology.

## DISCUSSION

The oxidation of iron from ferrous ( $\text{Fe}^{2+}$ ) to ferric ( $\text{Fe}^{3+}$ ) by the acidophilic iron bacteria is well documented. However, the role of bacteria in the reduction of iron from the oxidized ferric form to the reduced ferrous form of iron is unclear. The formation of siderite is known to occur when ferrous iron comes into contact with an excess of carbonate ions or by saturation with  $\text{CO}_2$  under anaerobic conditions. Work by Coleman et al., (1993) found that siderite was formed through the reduction of ferric oxides to ferrous iron by the sulfur reducing bacteria *Desulfovibrio desulfuricans* and the combination of this reduced ferrous iron with bicarbonate and hydroxide ions present in the sediments could produce siderite. It can be hypothesized that a concentration of ferric oxides could have occurred through the nucleation and subsequent concentration of oxidized  $\text{Fe}^{3+}$  by certain types of nonacidophilic bacteria known to concentrate ferric hydroxides  $\text{Fe}(\text{OH})_3$ , on their outer sheaths and/or cell walls. It is possible that the drying and concentration of Lake Gosiute at the Tipton/Wilkins Peak boundary led to more alkaline and saline conditions that may have caused the iron bacteria to be less prevalent and allowed for development of anaerobic mud flat conditions.

Bacteria or descendants of the bacteria may have come from two different bacterial groups; sheathed bacteria, represented by genera being *Sphaerotilus* and *Leptothrix* and the budding or appendaged bacteria with the representative genus *Gallionella*. *Leptothrix*, *Sphaerotilus*, and *Gallionella* bacteria are known to become encrusted with iron oxides, which can constitute up to 90% of the dry weight of the cell. Members of the Genus *Leptothrix* also have the ability to shed their iron encrusted sheaths and grow new sheaths in which 95% of the sheaths have been found to have no cells associated with them with the iron oxide encrusted sheaths continuing to act as nuclei for iron oxide precipitation. The presence of these types of bacteria in the lake before and during the drying and concentrating period could have served to concentrate soluble ferrous iron compounds into solid ferric oxide precipitates (Mason and Kirchner, 1994).

*Leptothrix*, *Sphaerotilus*, and *Gallionella* or their ancestral types have the ability to precipitate iron oxide, thus providing a strong line of evidence for the participation of bacteria in the formation of ferric oxide and ultimately siderite in sediments of the Green River Formation. Sheathed bacteria like the *Sphaerotilus* and *Leptothrix* genera or their ancestral types could have inhabited the waters of Lake Gosiute during Tipton time, immediately preceding the extreme drying of Wilkins Peak stage. Both *Sphaerotilus* and *Leptothrix* grow in waters containing high iron concentrations and are both tolerant to microaerophilic environments which probably existed in the shallow lake during this period. In this environment, ferric hydroxides/oxide deposits could serve as the substrate for the enzymatically mediated reduction of the ferric iron into the more soluble ferrous form by an organism such as *Desulfovibrio*, a sulphate reducing bacteria. Ferrous iron, in combination with bicarbonate and hydroxide ions, could be readily converted to siderite (Mason and Kirchner, 1994).

Mineralogical distribution and geostatistical data additionally support this scenario of biogenic formation of siderite. Siderite distributions at the Tipton/Wilkins Peak contact negatively correlate to the formation of all other carbonates, except for dolomite, and show a negative correlation to pyrite (Mason, in press). Negative correlation to pyrite would be expected when sulfur reducing bacteria reduce iron enzymatically, with pyrite as a by-product of  $\text{H}_2\text{S}$  production and subsequent  $\text{FeS}_2$  precipitation.

## CONCLUSIONS

Because the internal structure of the fossil bacteriamorphs was not observable, positive identification was not possible. However, the following criteria were employed to determine if the form was a possible bacteriamorph. These criteria were modified from those set forth by Westall (1999). These are: (1) Is the modern form found in an environment comparable with that of the Green River time? (2) Does the fossil bacteriamorph fall within the size range of the modern analog? (3) Does the fossil bacteriamorph have a similar shape, i.e. round, oval, rod-shape, curved, spiral or filamentous to the modern counterpart? (4) Does the fossil bacteriamorph have a cell wall that resembles its modern counterpart? (5) Modern bacteria, through reproduction generally form colonies. Was there evidence of colonial association in the fossil bacteriamorphs? (6) Is the composition of the fossil bacteriamorph what might be expected in Eocene sediments, i.e. has permineralization or mineral replacement occurred altering the chemistry, but not the general morphology of the fossil bacteriamorph. Fossil bacteriamorph forms which met all of these criteria were deemed as plausible to be considered fossil bacteria and were included in this work.

The fossil bacteriamorphs identified in this study of the Green River Formation display remarkable preservation. Although positive identification of the bacterium cannot be made due to mineral replacement of the original biological material, morphology of the fossil bacteriamorphs and direct comparisons to modern bacteria with regard to morphology and the environment in which they are found, can be drawn. These comparisons made, this evidence seems overwhelmingly convincing that ancient bacteria played a role, either minor or major, in the genesis of siderite in the Green River Formation.

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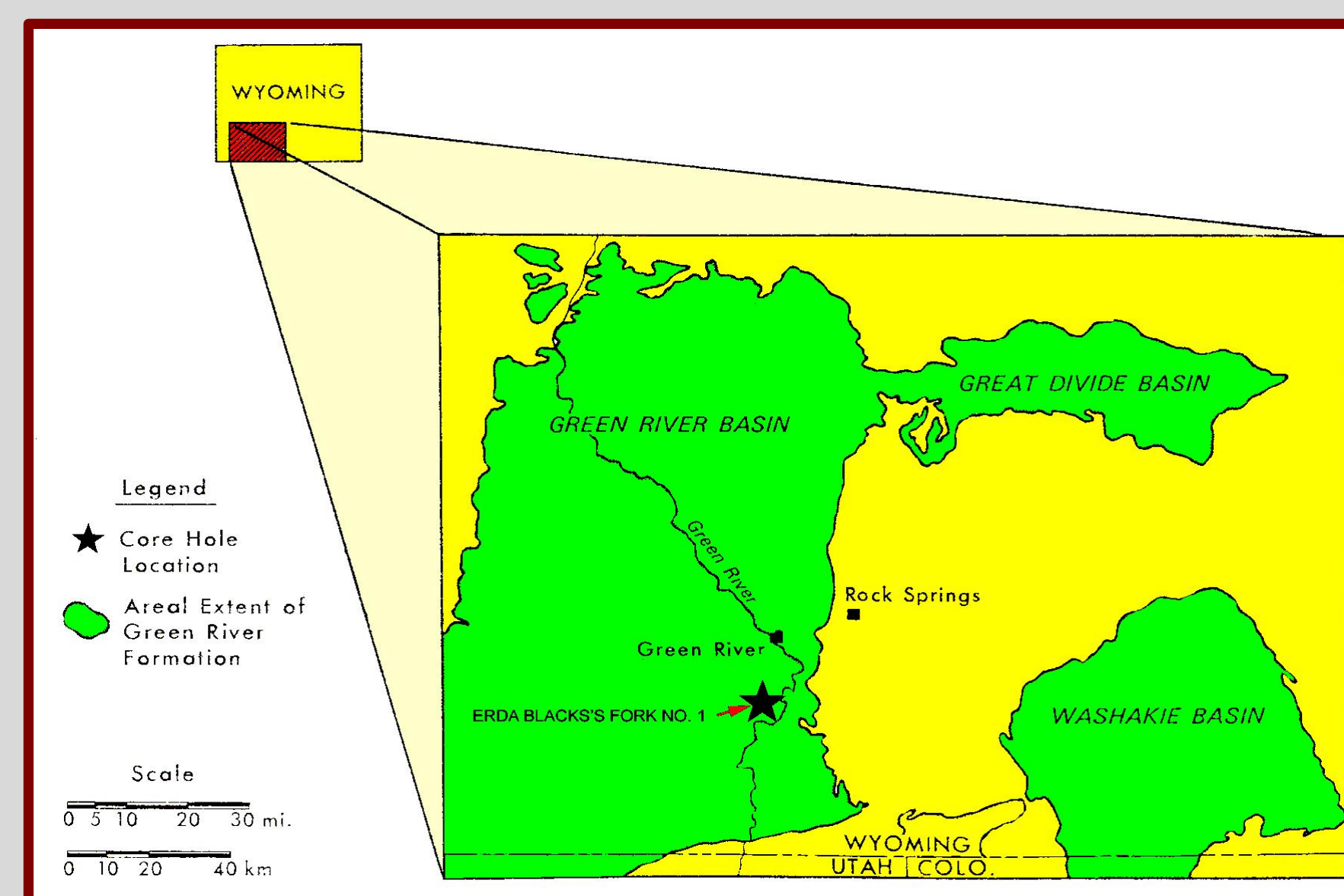


Figure 2. Areal extent of the Green River Formation in Wyoming and the location of ERDA Black's Fork No. 1 core hole.

## DISTRIBUTION OF SIDERITE

Siderite  $\text{FeCO}_3$  and Mg-siderite  $(\text{Fe,Mg})\text{CO}_3$  occur sporadically in the sediments of the Green River Formation of Wyoming. A distinct increase in abundance of siderite can be observed at the Tipton/Wilkins Peak contact throughout ten core holes of the Green River Basin (Mason, in press). Geostatistical analyses comparing the abundance of siderite to other minerals, shows a strong negative correlation with calcite, a moderate positive correlation with dolomite, and a strong positive correlation with pyrite and silicate minerals. This information suggests that siderite genesis may be related to conditions other than the normal lacustrine carbonate-forming conditions; with the moderate correlation of siderite to dolomite resulting as an artifact of the contribution of mudflat sediments being washed into the lake. The strong positive relation of siderite and pyrite strongly suggests a relationship related to the availability of iron. The lake-wide occurrence of siderite defines the boundary that marked the change in geochemical conditions between the fresher waters of the Tipton Member into the more evaporative and saline waters of the Wilkins Peak Member. This change represents a major climatic or circulation change of Lake Gosiute with the "drying up" of the lake at the end of Tipton time and followed by the evaporative conditions of Wilkins Peak time (Mason, in press). Figure 3 illustrates the distribution of siderite, defined by XRD peak height, and the lithology of the U.S. ERDA Black's Fork Core Hole No. 1. The discovery of three fossil bacteriamorphs is presented as evidence to support the hypothesis that siderite genesis in Lake Gosiute may have been related to bacterial action. Figure 3, Image A is an SEM image of a filamentous fossil bacteriamorph that has a morphology similar to several bacteria in the modern *Desulfovibrio* family. For comparison, an SEM photograph of a modern *Desulfovibrio* is shown. Figure 3, Image B is an SEM image of another filamentous fossil bacteriamorph that has a morphology that strongly resembles the modern sheathed *Leptothrix* family of bacteria, which can be found in modern aquatic, organic-rich environments and is known to oxidize iron. For morphological comparison. An optical photograph of the modern bacterium *Leptothrix* is shown. The fossil bacteriamorph in Figure 3, Image C was found in direct proximity to siderite and has a morphology that is striking similar to modern fresh water iron-oxidizing bacteria. For comparison, an SEM photograph of the modern filamentous fossil bacteria *Leptothrix* is shown.

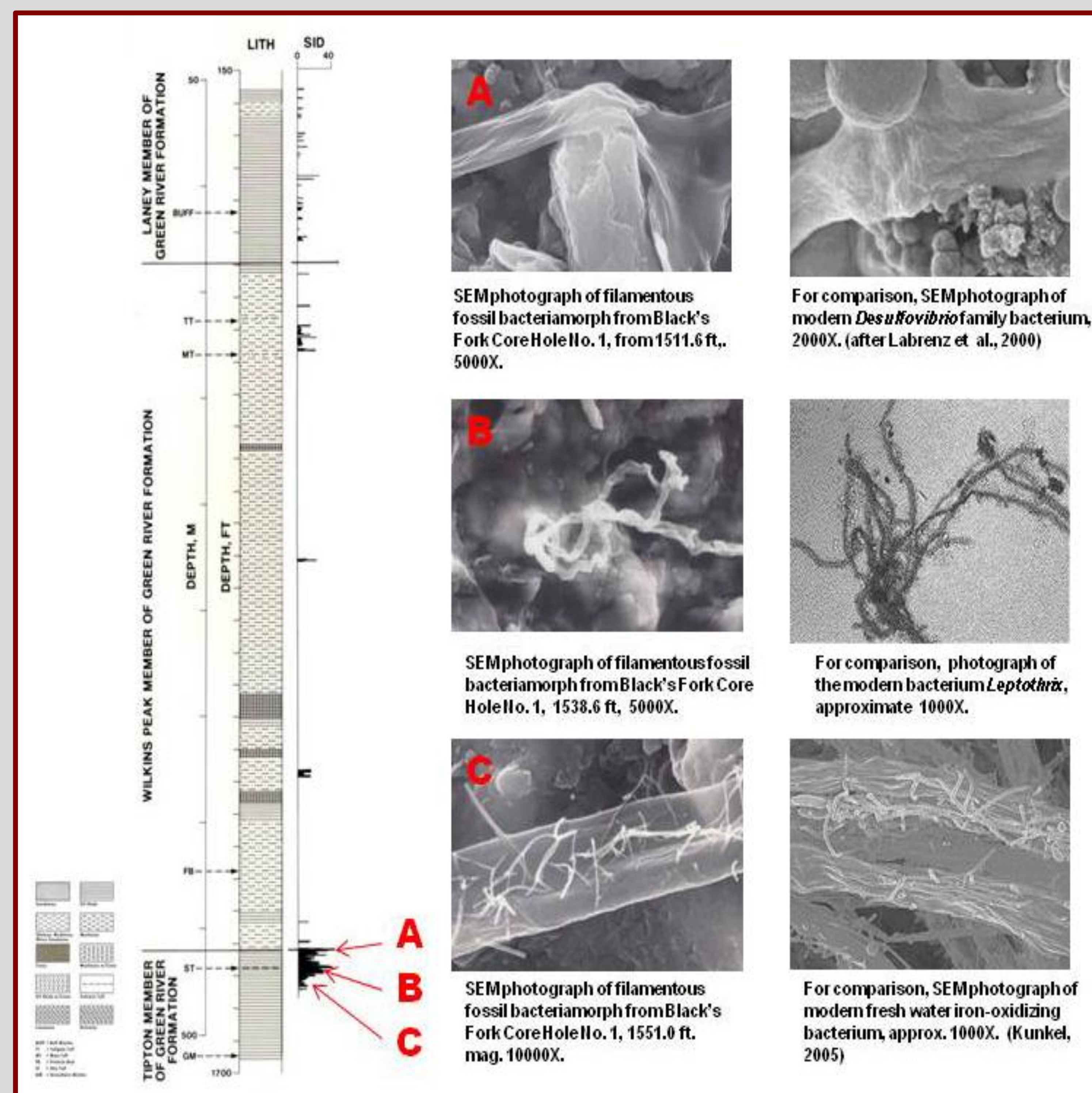


Figure 3. U.S. Energy Research and Development Administration/Laramie Energy Research Center Blacks Fork core hole No. 1 with the lithology, formational contacts, and XRD peak heights of siderite indicated. Location of samples from which SEM photomicrographs of bacteriamorphs indicated as A (1511 ft.), B (1538 ft.) and C (1551 ft.) indicated.