

Drainage-line silcrete in the Athabasca Oil Sands deposit: Evidence for Early Cretaceous hypogene anhydrite-halite dissolution and brine seeps to the surface

Paul L. Broughton

Broughton and Associates

Abstract

The Beaver River drainage-line silcrete consists of tens of kilometer long linear trend of discontinuous caprocks distributed along the floor of the Athabasca River Valley in northern Alberta. The silcrete developed within unconsolidated fluvial sand beds of the McMurray Formation, the host rock of the Cretaceous Athabasca Oil Sands. Early stage silicification processes occurred toward the end of lower McMurray (Aptian) deposition, responsive to regional dissolution of halite-anhydrite beds in the Middle Devonian Prairie Evaporite only 200 m below. Sulphate-saturated brines migrated up-section into the uppermost sand beds of the lower McMurray at topographic lows along a segment of the Assiniboia PaleoValley, which represents the ancestral trend of the Quaternary-age Athabasca River Valley. Redox by sulphate-reducing bacteria associated with the extensive lower McMurray Formation peat mires resulted in strongly acidic groundwater with increased silica-saturation. At the onset of middle McMurray deposition, this new geographic setting resulted in oxygenated river water coming in contact with the silica-saturated acidic groundwater along topographic lows of the Assiniboia PaleoValley. This shift in pH triggered silica cementation in the sand beds along the margins of the river valley, resulting in the formation of the Beaver River silcrete. This drainage-line silcrete genesis event resulted from an unusual combination of voluminous sulphate-saturated brine seeps to surface and pervasive microbial induced redox.

Introduction

The Lower Cretaceous McMurray Formation in northeastern Alberta, western Canada, hosts the reservoir rocks of the Athabasca Oil Sands (Hein et al., 2000, 2001, 2013; Hein, 2015). These bitumen-saturated quartz sand, as much as 150 m thick, have a tripartite stratigraphy represented by a lower interval of fluvial sand and overbank kaolin and lignite continental deposits, disconformably overlain by a middle interval of fluvio-estuarine sediments including innumerable multi-kilometer-long point bars, and an upper interval with increasingly marine-influenced sand parasequences. These unconsolidated fluvial and fluvio-estuarine sand reservoirs trapped hydrocarbons that migrated to the area toward the end of the Cretaceous or early Paleogene. Biodegradation *in situ* resulted in a bitumen-saturated interval as much as 130-150 m thick and extending across 46,000 km². Stratigraphically positioned at the top of the lower interval of the McMurray bitumen-saturated sand is a silcrete bed as much as 1.7 m thick. This silcrete is referred to as the Beaver River sandstone or quartzite.

Partial erosion of this silicified bed and the overlying middle McMurray Formation strata occurred with the Late Pleistocene expansion of the Athabasca River Valley. An outburst-

flooding event occurred as the northwest arm of the glacial Lake Agassiz exposed and partially eroded Beaver River quartzite along the river valley floor (Fisher, 2007; Kristensen et al., 2016). This incision of the Athabasca River into the Athabasca Oil Sands resulted in this silcrete at the top of the lower interval forming a narrowly constrained and linear alignment of disconnected outcrops along the length of the river valley. These siliceous caprocks are discontinuous and rapidly pinch-out after only a few to tens of meters (Fig. 1). Partial erosion of the drainage-line silcrete sourced the distribution of innumerable quartzite boulders for tens of kilometers along the floor of the river valley (Fig. 2).



Figure 1. Late Pleistocene expansion of the Athabasca River Valley exposed the silcrete bed at the top of the lower McMurray Formation. Partial erosion of the Beaver River Sandstone resulted in distribution of silcrete caprocks and dispersal of quartzite boulders along the Athabasca River Valley and across the Bitumount Trough floor. This example of a Beaver River silcrete caprock is located adjacent to the Quarry of the Ancestors.

This review interprets the linkage between salt dissolution processes in underlying Middle Devonian evaporite strata only 200 m below with the morphogenesis of a meter thick silicified interval within a succession of otherwise unconsolidated Cretaceous sand. Aspects of the process resulted in the localization of the quartzite to a singular stratigraphic horizon, subsequently exposed along the length of the Athabasca River Valley in northeast Alberta, but not elsewhere. More recent research has demonstrated the spatiotemporal linkage between the

formation of the Beaver River Sandstone as a silcrete bed that was responsive to a linear trend of concurrent halite-anhydrite dissolution and migration of sulphate-saturated brine seeps up-section to the margins of the overlying river valley (Tsang, 1998; Broughton, 2020). This resulted in the morphogenesis of a drainage-line silcrete responsive to a unique combination of hypogene ascent of sulphate-saturated brine seeps and microbial redox activity in groundwater associated with pervasive peat mires accumulate as the uppermost deposits of the lower McMurray Formation.

Study Area and Geo-archeology

The distribution of the Beaver River Sandstone is limited to areas where beds of the lower and middle McMurray Formation have been exposed at the surface along the length of the Athabasca River Valley. The silcrete occurs as a discontinuous series of outcrops that are narrowly and linearly distributed along the Athabasca River Valley floor (Fig. 2), and as concentrations of widely dispersed boulders where the valley floor widens upon the intersection with the 100 km long Bitumount Trough, the largest known salt dissolution-collapse structure (Broughton, 2013, 2015).

Exposure of the silcrete bed along the walls and floors of the Athabasca River Valley attracted prehistoric aboriginal groups because the material was used for local manufacture of arrowheads, axes and pounding tools (Fenton and Ives, 1982, 1984, 1990; Ives and Fenton, 1983, 1985; Kristensen et al., 2016). There is an extensive geo-archeological literature on the hundreds of quarry sites and workshops identified along the Athabasca River Valley and tributaries (Fig. 2). The most significant quarries are the Beaver River Quarry and the nearby Quarry of the Ancestors. Each of these is a cluster of as many as 80 excavation pits (Kristensen et al., 2016). Samples of the Beaver River quartzite used in this study were collected from outcrops adjacent to the Quarry of the Ancestors (Fig. 1).

Geologic Setting

Deposits of the McMurray Formation (Aptian), the reservoir of the Athabasca Oil Sands, accumulated unconformably on Middle-Upper Devonian strata in northeastern Alberta (Hein et al., 2001, 2013; Hein and Cotterill, 2006; Hein and Marsh, 2008; Hein, 2015; Broughton, 2017a, 2017b; Hein and Dolby, 2018). The Devonian strata include the pre-erosion thickness of as much as 200 m of the Prairie Evaporite Formation, the upper Elk Point Group. These salt beds, consisting of halite and subordinate anhydrite, accumulated along the Elk Point evaporite basin that extended across western Canada (Holter, 1969; Grobe, 2000; Broughton, 2018) and into areas of eastern Montana and western North Dakota (LeFever and LeFever, 2005).

Middle Jurassic-Early Cretaceous Cordilleran orogenic movement resulted in partitioning of the Western Canada Sedimentary Basin into the Alberta Basin to the northeast and the adjoined Williston Basin to the southwest, separated by the Sweetgrass Arch in northeastern Montana and its extension into Alberta as the Bow Island Arch. Most post-Devonian Paleozoic strata were eroded across northeastern Alberta. The Athabasca Oil Sands, mostly represented by the McMurray Formation, accumulated on carbonates of the Middle-Upper Devonian Beaverhill Lake Group. The salt beds of the Prairie Evaporite are only 200 m below this sub-Cretaceous unconformity surface. As much as 130 m of partially to complete removal of the salt interval occurred in the northeastern Alberta Basin, in contrast with regional areas having up to 200 m of

complete salt removal across the southern Saskatchewan area of the northern Williston Basin (Holter, 1969; Meijer Drees, 1994; Grobe, 2000; Broughton, 2013, 2015, 2018; Hein et al., 2013; Hauck et al., 2017; Hauck, 2020). These regional salt removal patterns developed during the Late Jurassic to Early Cretaceous Cordilleran tectonism of the Alberta Basin. Removal patterns during Antler and Laramide orogenic deformation history characterize the Williston Basin to the southeast. The two regional-scale salt dissolution trends are 100-150 km wide, extend for 100s of kilometers within the Prairie Evaporite strata, resulting in the largest known hypogene evaporite karst collapse. One of these major trends extends for 1,000 km along the eastern up-dip margin of the adjoining Alberta and Williston Basins, and coincides with the eastern margin of the Western Canada Sedimentary Basin. A 300 km long segment of this salt removal trend is only 200 m below the Athabasca Oil Sands deposit.

Stages of salt removal were initiated during the Cordilleran tectonism and continued into the Aptian concurrent with deposition of the McMurray Formation (Broughton, 2013). The salt removal resulted in extensive collapse areas of the overlying Middle-Upper Devonian strata, configuring the sub-Cretaceous unconformity that floors the McMurray Formation deposits. Salt removal stages resulted in collapse structures that vary in size from sinkholes to 100 km long collapse troughs (Broughton, 2013). The 100 km long V-shaped Bitumont Trough is the largest of the salt removal-collapse structures. It was developed during the deposition of the lower interval of the McMurray Formation below the northern area of Athabasca Oil Sands.

The salt scarp represents the westward migrating salt dissolution front approximately 200 m below the lower McMurray Formation sediments. The salt scarp is a 10-20 km-wide regional trend of partial dissolution that separates areas of complete salt removal to the east from undisturbed beds to the west (Grobe, 2000; Hein et al., 2013; Broughton, 2013). The continental sand dominated deposits of the lower interval and the fluvio-estuarine sediments of the middle-upper McMurray intervals were distributed along a northern Alberta segment of the Assiniboia PaleoValley on the Devonian paleotopography, following the structural low trend paralleling the eastern margin of the underlying salt scarp. Overprinting this trend, the Quaternary development of the Athabasca River Valley similarly followed the underlying Assiniboia PaleoValley, the ancestral course of the Athabasca River Valley along the eastern margin of the salt scarp.

The halite-anhydrite dissolution front underlying the Athabasca deposit resulted in parallel dissolution trends responsive to differing mineral solubility rates as the dissolution front migrated westward (Fig. 3). For example, easternmost areas have complete removal of all halite and anhydrite beds. Westward of areas with complete removal, partial removal of the halite with preservation of the anhydrite occurred, whereas complete removal of the halite and partial removal of the anhydrite further to the west. These trends contrast with westernmost areas that were unaffected by dissolution and preserve a mostly complete salt section. Importantly, the ancestral Athabasca River Valley and coincidental trend of the Beaver River Sandstone overlie the zone of complete halite removal with partial anhydrite removal (Broughton, 2013, 2015, 2016; Schneider and Grobe, 2013; Schneider et al., 2013, 2014).

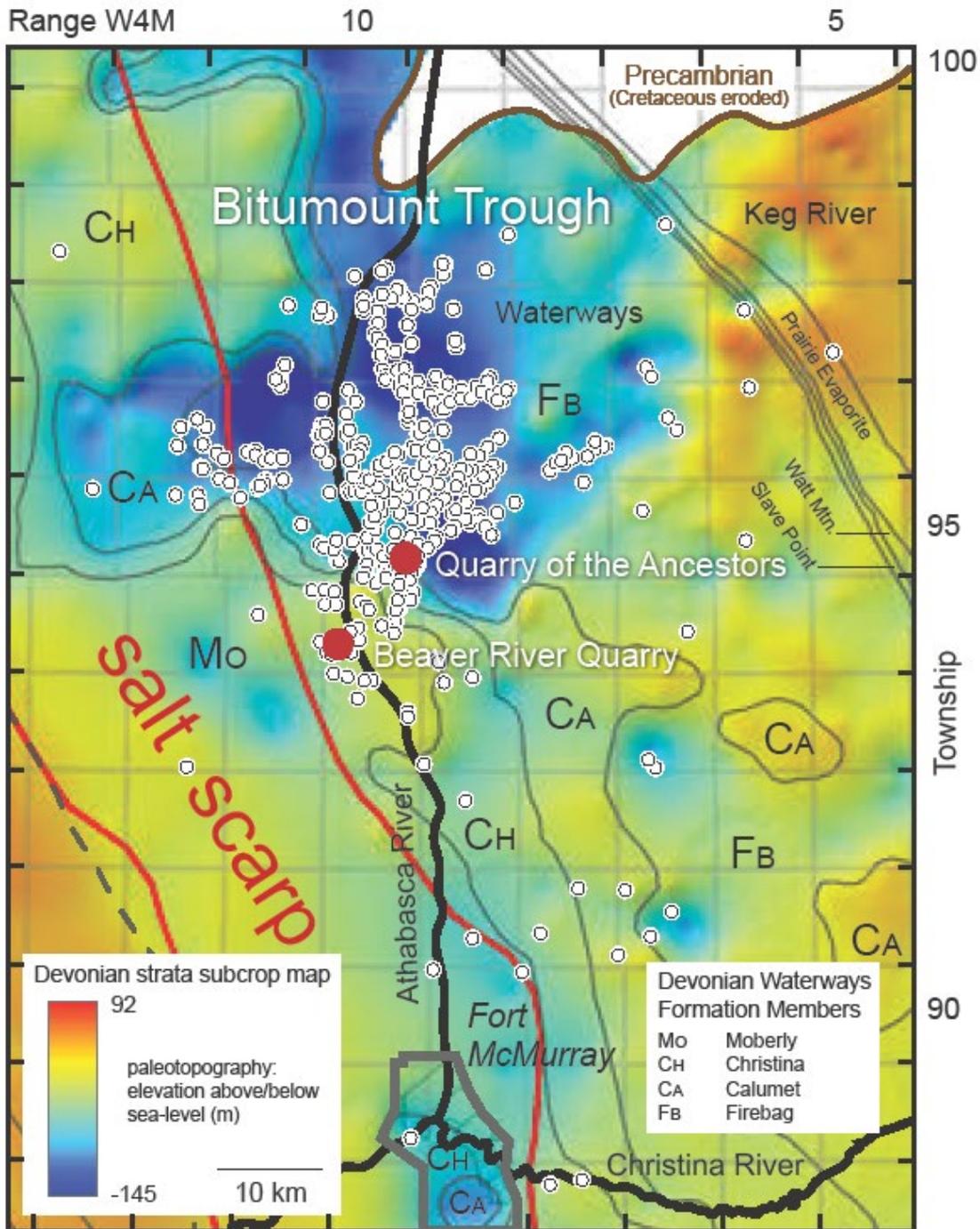


Figure 2. The Beaver River Sandstone consists of quartzite outcrops and boulders dispersed along the Athabasca River Valley and its intersection with Bitumount Trough floor. This drainage-line silcrete trend follows the underlying Prairie Evaporite salt scarp, 200 m below. Modified from Broughton (2015), Hauck et al. (2017), and Kristensen et al. (2016).

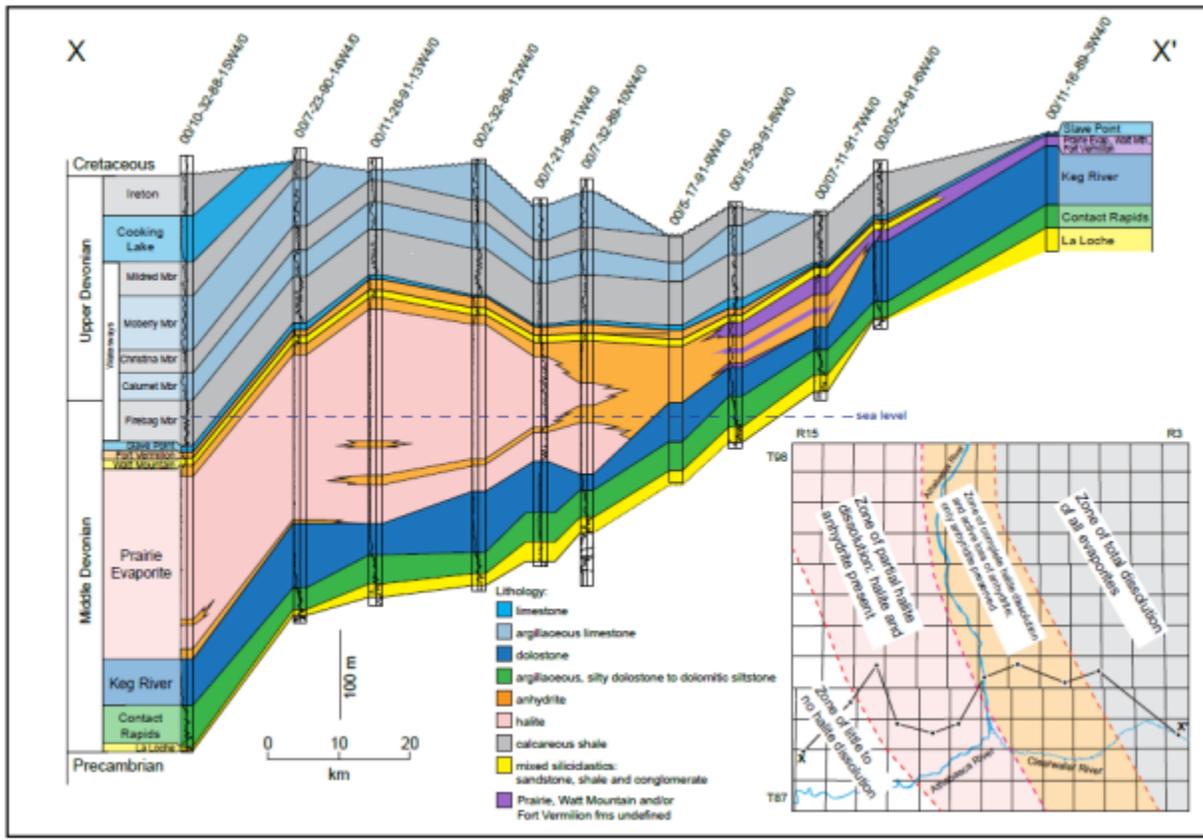


Figure 3. Devonian strata below the Cretaceous Athabasca Oil Sands. Westward migration of the salt scarp below the northern Athabasca deposit was concurrent with deposition of lower McMurray sediments and resulted in variable removal of salt beds consistent with mineral solubility. Complete removal of the salt beds occurred to the east and undisturbed beds to the west of these partial dissolution trends. The drainage-line silcrete trend follows the Athabasca River Valley and underlying segment of the Assiniboia Paleovalley on the Devonian paleotopography. These overlying river valleys follow a portion of the underlying NW-oriented salt scarp where complete halite removal and incomplete removal of less soluble anhydrite occurred. Modified from Schneider and Grobe (2013) and Schneider et al. (2013, 2014).

Description of the Silcrete

The strongly indurated Beaver River Sandstone is pebbly orthoquartzite consisting of 75-95% quartz grains and 5-25% quartz pebbles, which are mostly less than 1 cm in diameter. The silica cement consists of overgrowth on detrital quartz grains with additional pore-filling by subhedral microcrystalline quartz fabrics and anhedral or euhedral quartz micro-crystals (Fig. 4A, B). The clay content of the quartzite, mostly gibbsite and minor illite, occurs in trace amounts and as dust rims of the quartz overgrowths. These dust rims consist of curvilinear trains of opaque clay particles and small voids less than 1-2 microns readily observable with SEM imaging. Partial

dissolution of the quartz grains was pervasive but not volumetrically significant. The fluid-filled inclusions in the cement are very rare and very small, less than 0.5 microns.

The quartzite cement is characterized by the pervasive distribution of silicified microbial filaments consisting of branching hollow sheaths with diameters of 3-4 microns (Fig. 4C, D). These fossilized bacteria of unknown taxonomic affinity are interpreted as widespread sulphate-reducing microorganisms responsible for increased acidity in groundwater, leading to environmental conditions necessary for the silcrete genesis. These fossilized tube-form bacterial sheaths are observed in relict porosity. They were also preserved as trains of micro-void artifacts enveloped by the quartz overgrowth cement (Fig. 4A, B). The exterior surfaces of these tube-like filaments are covered with bulbous micro-scale (0.2-0.6 microns) protuberances (Fig. 4D). XRD of the quartzite indicates the presence of opal in trace amounts. Broughton (2020) reported on the application of nuclear magnetic resonance (NMR) with and without magic angle spinning methodology (MAS NMR) to determine the crystalline state of these silicified microbial filaments, and further understand transition from opaline to microcrystalline α -quartz of a silcrete. The results indicate that the bulbous non-crystalline protuberances consist of amorphous hydrated silica but have incipient developments of nanoscale crystallite faces, less than 0.6 microns, coexisting with the bulbous non-crystalline protuberances. These preserve a stepped transition phase from opal-CT (Q_3) to a more crystalline structured quartz (Q_4 /near Q_3) at the nanoscale. No preservation of opal-A ($\sim Q_2$) was recognized. The tubular microfossil structures formed of mixed opaline silica and a stepped phase transition into a higher ordered crystalline phase (cristobalite $\sim Q_4$ /near Q_3) as the hydrogen bonds were removed.

Modern Analogue for Cretaceous Brine Seeps to Surface

Various segments of these regional salt removal patterns were reactivated during the Quaternary as glacial meltwater flows into the shallow subsurface came in contact with the Prairie Evaporite. The meltwater flows removed the uppermost salt beds of the Prairie Evaporite, resulting in surface discharges as saline springs along the Athabasca River Valley (Borneuf, 1983; Jasechko et al., 2012; Gibson et al., 2013). The meltwater flows into the shallow subsurface resulted in tens of km² Pleistocene collapse structures across the southern Saskatchewan area of the northern Williston Basin, but without similar collapses in the Alberta Basin. Nevertheless, saline brines discharged at the surface occur along topographic low trends in both the Alberta and Williston Basins.

There is strongly linear trend of elevated TDS in the groundwater that occurs along the Athabasca River Valley (Fig. 5), which is consistent with a mixture of subglacial meltwater having contact with the underlying salt scarp, followed by saline water and brine migrations up-section (Broughton, 2020). The geochemistry of brine springs along the Athabasca River Valley record a wide range of measurements responsive to variations in the mixture of glacial meltwater, dissolved salts, and meteoric-sourced groundwater (Fig. 5). These analyses vary from near fresh water (240 mg/L) to saline water and brines (280 g/L) (Borneuf, 1983; Grasby, 2006; Gibson et al., 2013; Cowie, 2015; Cowie et al., 2015). The range of TDS in groundwater samples commonly exceed 72,000 mg/L and often as much as 100,000 mg/L or more. The regional distribution patterns of elevated TDS measurements are similar to measurements of halite-sourced stable isotope ratios in McMurray Formation waters and samples of surface-discharged seeps, regardless of having been mixed with influxes of fresh subglacial meltwaters.

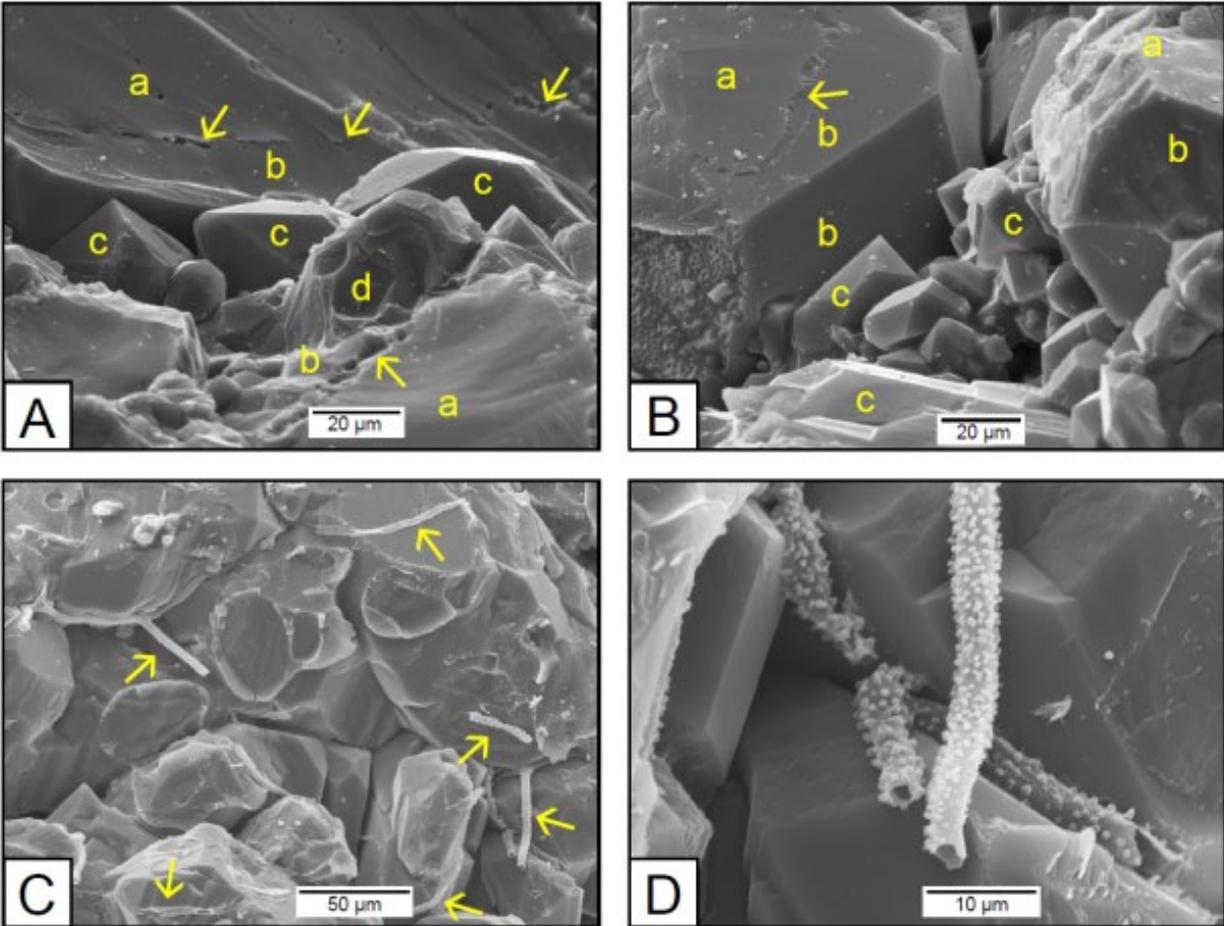


Figure 4. SEM imaging of siliceous cement. (A-B) Detrital quartz grains (a) and cement overgrowth (b). Trains of micro-voids wrapped around detrital sand grain surfaces (arrows). Cement incompletely filled the hollow microbial filament sheaths, resulting in curvilinear trains of micro-porosity consistent with the microbial filaments wrapped around sand grains (arrows). Elsewhere porosity between the sand grains and cement overgrowth was partially infilled by euheedral quartz crystals (c). (C-D) Silicified microbial filaments (arrows) consisting of tubular sheaths covered with bulbous micro-protuberances of opaline silica in stepped transition to nanoscale-crystalline silica (cristobalite).

Brines discharged at the surface characteristically have elevated H_2S in solution (Borneuf, 1983; Grasby, 2006). High sulphate concentrations in spring waters have $\delta^{34}S$ values in dissolved sulphate that varies from 15‰ to 20‰, which is consistent with values for the Prairie Evaporite (Grasby, 2006). For example, a brine seep flow into La Saline Lake on the east bank of the Athabasca River north of Fort McMurray has a high sulphate content sourced from the dissolution of anhydrite beds at depth. TDS measurements from this spring typically record 73,200 mg/L (Ca 1830 mg/L; Mg 456 mg/L; Na 25,600 mg/L; SO_4 4,780 mg/L; Cl 40,200 mg/L). Other researchers report seasonally dependent measurements with a wide range of TDS

measurements, such as 44,700-51,800 mg/L (Borneuf, 1983; Gue et al., 2015; Birks et al., 2018). Microbial sulphate reduction occurs near surface and results in spring water affected by methanogenesis and methane oxidation. Muds with elemental sulfur occur near the spring. Other springs along the Athabasca River Valley also have elevated sulphate content, but the La Saline brine spring has as much as 8x the level of others.

The brine geochemistry indicates Quaternary dissolution of both halite and anhydrite beds in the underlying Prairie Evaporite. This process is interpreted as a modern analogue for more extensive of anhydrite dissolution toward the end of the lower McMurray deposition, resulting in voluminous sulphate-saturated brines that migrated 200 m up-section into sand beds along the margins of the overlying Assiniboia PaleoValley, subsequently incised by the paralleling Quaternary trend of the Athabasca River Valley.

Sulphate Redox and Genesis of the Drainage-line Silcrete

The transition from an unconsolidated quartz sand to a quartzite necessitated infilling of the original porosity (~25-30 %) by silica cement. Silica sourced from corrosion of the lower McMurray quartz sand was insufficient for this process. In contrast, voluminous silica in solution was sourced from breakdown of aluminosilicate clays under increasingly acidic conditions of peat mires developed throughout the uppermost interval of the lower McMurray strata. The constrained corrosion of the quartz sand grains and kaolin alteration was permitted by concurrent microbial redox of the up-section migrating sulphate-saturated brines, an event that occurred toward the end of lower McMurray deposition. As a result, silica-saturated acidic groundwater from the alteration of kaolin beds in addition to the modest quartz grain corrosion can account for sufficient dissolved silica necessary for cement volumes necessary to plug the sand porosity (Broughton, 2020).

A shift of the broadly acidic groundwater toward a neutral pH occurred in the silica-saturated groundwater with the entrenchment of the axial channel belt upon the onset of the earliest middle McMurray fluvial sedimentation. Sand cementation occurred as the silica-saturated groundwater come in contact with oxygenated groundwater along the margins of the river channel. This shift in pH triggered the precipitation of silica cement along a less than 2 m thick narrow trend of uppermost lower McMurray sand beds, and may have included some pebble-rich channel lags. This silicification trend was a narrowly linear zone that extended intermittently for tens of kilometers, resulting in a drainage-line silcrete along topographic lows of the Assiniboia PaleoValley and across the width of the Bitumount Trough. The resulting Beaver River quartzite bed was exposed and partially eroded during the Late Pleistocene expansion of the Athabasca River Valley, resulting in silcrete caprocks and dispersal of quartzite boulders along the valley floor.

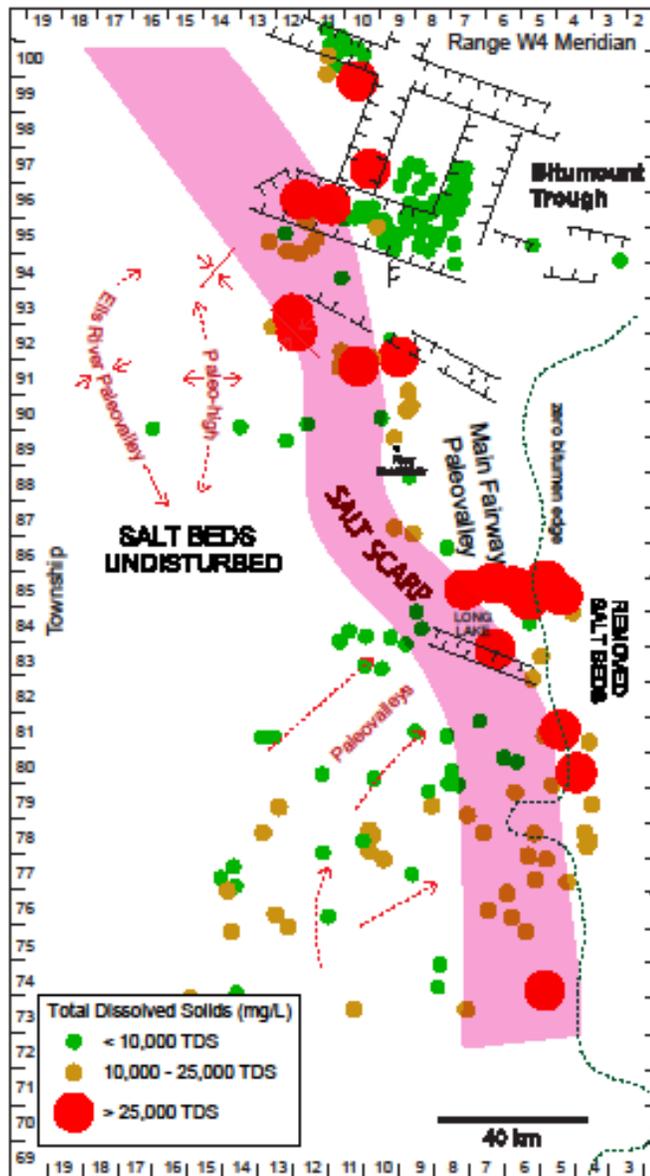


Figure 5. The Prairie Evaporite salt scarp below the Athabasca River Valley, resulting in salt collapse troughs up to 100 km long. The westward-migrating salt scarp represents a 10-20 km wide trend of incomplete salt dissolution that separated areas of complete salt removal to the east from undisturbed beds to the west. Measurements of Total Dissolved Solids of near surface formation water and meteoric-charged groundwater mixed with saline seeps discharged at the surface. Measurements of elevated TDS follow the regional NW-oriented trend of the underlying salt scarp. Most salt removal occurred during the deposition of the McMurray Formation, but Quaternary dissolution activity continued at a substantially reduced rate and resulted in brine springs and saline lakes along the Athabasca River Valley. Modified from Broughton (2013, 2015, 2017a, 2017b) with TDS patterns from Cowie (2013) and Cowie et al. (2015).

Conclusions

The morphogenesis of the Beaver River silcrete occurred because there were voluminous sulphate-saturated brine seeps that migrated up-section to the margins of the ancestral Athabasca River Valley toward the end of the lower McMurray deposition. The brine seep mixed with acidic peat mire groundwater, resulting in the pervasive spread of microbial mats and sulphate redox that silica-saturated the groundwater. Silicification was subsequently triggered as the pH shifted as the silica-saturated groundwater mixed with oxygenated river water at the onset of middle interval deposition. The drainage-line silcrete pattern was controlled by spatiotemporal of a significant halite-anhydrite dissolution event that occurred along the salt scarp at the time of the uppermost lower McMurray deposition. This halite-anhydrite dissolution and brine migration up-section event were coincidental with reconfiguration of the sub-Cretaceous structure flooring the Athabasca deposit and the subsidence-collapse of the Bitumount Trough. Without this unusual combination of sulphate-saturated brine seeps to surface and pervasive microbial induced redox, the depositional conditions for both lower and middle McMurray Formation strata would not have been unusual and no silcrete would have formed.

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