QUANTITATIVE MINERALOGY AND DISTRIBUTIONS OF MINERALS OF THE GREEN RIVER FORMATION, PICEANCE CREEK BASIN, WESTERN COLORADO

by

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ABSTRACT

Over thirty-five minerals have been identified in the Green River formation of the Piceance Creek Basin, using quantitative X-Ray Diffraction (XRD) bulk analysis. Fifteen major phases occur at over 5 wt% average in 117 samples spanning the thickness of the formation. Integrated data from cores, outcrops, and the USGS represent two lacustrine depositional environments: basin margin shallow-water and basin center deep-water. Results are presented in a stratigraphic framework of six lake stages. Mineral distributions support a permanently stratified saline lake model characterized by a chemocline that separates a less saline upper water layer from a more saline, alkaline, and reducing lower water layer. Lateral and vertical variations in salinity, alkalinity, redox conditions, silica and CO₂ activities, and depths of the water column and chemocline are proposed to have permitted localized differences in precipitation, preservation, alteration, and formation of authigenic phases across the meromictic lake. Original detrital mineral components contributed to the basin included mainly quartz, clay minerals and feldspars. Reversal of weathering reactions during periods of extreme water chemistry converted clay minerals to authigenic feldspars and other authigenic phases.

Distinct assemblages of authigenic minerals differ between the basin center and basin margin locations. Basin center samples are enriched in buddingtonite ((NH₄)AlSi₃O₈*0.5H₂O), and the saline minerals nahcolite (NaHCO₃), dawsonite (NaAl(CO₃)(OH₂)), and halite (NaCl). Only trace quantities of saline minerals occur in the basin margin samples, instead, high quantities of the zeolite, analcime (NaAlSi₂O₆*H₂O), are found. Basin center samples are clay-poor (10 wt% ave), and organic matter-rich (12 wt% ave). Basin margin samples are clay-rich (24 wt% ave) and relatively organic matter-poor (7 wt% ave). Carbonate minerals represent a large proportion of GRF rocks, and are especially iron rich. Calcite and aragonite form only 12 wt% ave of total carbonates in the basin center.

Major changes in relative mineral proportions and assemblages occur in the basin center at two transition zones, which divide the stratigraphic column into three distinct mineral units. The lower mineral unit is richest in quartz, clay minerals, ferrodolomite, and calcite. The lower transition zone is characterized by decreases in clay mineral and quartz quantities, and increases in dawsonite, feldspars, and buddingtonite. The middle mineral unit is mainly composed of
nahcolite, dawsonite, feldspars, and ferrodolomite and represents the most saline period of lake history. The upper transition zone is characterized by a marked reduction in the occurrence of dawsonite, another increase in feldspar, a second decrease in quartz, decrease in buddingtonite, and increase in clay minerals. The major phases in the upper mineral unit are feldspars and ferrodolomite, with increased contributions by analcime and calcite.

Quantitative and qualitative relationships between minerals are suggestive of reactions responsible for authigenic mineral formation and differences in distributions due to local depositional conditions. Occurrences of nahcolite and analcime are mutually exclusive, pointing to distinct conditions of formation controlled by alkalinity, salinity and silica activity. Quartz and dawsonite exhibit a positive quantitative relationship in saline lake stages, resulting from a decrease in silica activity, and increase in salinity and alkalinity. Buddingtonite and ferrodolomite both show qualitative correlations with indicators of redox conditions.

Sample rock types in the basin margin include fine sandstone, siltstone, mudstone and marlstone. Rock types represented by samples in the basin center include siltstone, mudstone, marlstone, and saline subaqueous evaporite. The majority of siltstone and sandstone samples are arkosic, and most mudstone samples are feldspathic in both basin locations. A rock type classification based on grain size and relative quantities of 4 main mineral groups (saline minerals, Ca-Mg-Fe carbonates, framework silicates, and sheet silicates) reveals that dawsonite and buddingtonite quantities are not similarly distributed in the same rock types as other minerals of the same group.
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LIST OF ABBREVIATIONS

Carb .................. Divalent Carbonate Minerals
CEC .................. Cation Exchange Capacity (analysis for clay minerals)
CO-1 .................. Colorado Core Hole No. 1Section used for comparison data
Corg .................. Organic Carbon (as opposed to carbon in carbonate minerals)
COSTAR .......... Center for Oil Shale Technology and Research
CR-2 .................. Oil Shale core used for comparison from Dean, Pitman and Harrach, 1981
DP .................. Douglas Pass Outcrop Sections
EDS .................. Energy Dispersive X-Ray Spectroscopy (SEM-EDS)
Fsp .................. Feldspar
Ft .................. Feet
GRF ................. Green River Formation
ICP-MS .............. Inductively Coupled Plasma – Mass Spectrometer
IR .................. Infrared Spectroscopy
I/S .................. Illite / Smectite Clay Minerals
JS .................. John Savage 24-1 Core Section
MU .................. Mineral Unit
L1, L2, L3 .......... Lean Zone 1, Lean Zone 2, Lean Zone 3.....
OES .................. Optical Emission Spectroscopy
PCB .................. Piceance Creek Basin
Qtz .................. Quartz
R1, R2, R3 .......... Rich Zone 1, Rich Zone 2, Rich Zone 3.....
R/L .................. Rich / Lean Zones
S1, S2, S3 .......... Lake Stage 1, Lake Stage 2, Lake Stage 3 ..... 
SB .................. Sequence Boundary
SE .................. Secondary Electrons (as opposed to backscatter SEM image)
SEM ................. Scanning Electron Microscope
SRA .................. Source Rock Analyzer
TOC .................. Total Organic Carbon
USBM ............... United States Bureau of Mines
USGS .............. United States Geological Survey
wt% ave ............... Weight Per Cent Average (XRD Mineral Quantities)
XRD ................. X-Ray Diffraction Analysis
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...... do I get an honorary psychology degree with this?

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CHAPTER 1
INTRODUCTION

The Green River Formation (GRF) of western Colorado, northeastern Utah and southwestern Wyoming has attracted great interest for its rich oil shale and unique economic mineral resources. In the Piceance Creek Basin (PCB – also commonly referred to as the Piceance Basin) in Western Colorado, the GRF is the richest known oil shale in the world, making it a target for exploration and research into production and exploitation of oil shale resources (Figure 1.1) (Dyni, 2006; Johnson et al., 2010). Within the PCB, the GRF ranges in thickness from approximately 3000 feet in the basin center to 1000 feet in the basin margin (Tänavsuu-Milkeviciene and Sarg, 2012). The GRF is renowned for its impressively large concentrations of many unusual minerals, including rare sodium carbonates, and the discovery of minerals which were known only to exist in the GRF (Milton, 1971; Smith, 1983; Mason, 2007). Unusual minerals which usually occur only in minor, localized deposits around the world were formed in vast, pervasive layers in the GRF (Smith, 1983). The assemblages of authigenic and diagenetic minerals are distinct in each basin that the GRF deposited (Figure 1.1) (Smith, 1983). The GRF of the PCB has the richest organic content (up to 45% TOC) in stratigraphic sections which have the highest concentrations of rare saline minerals (Robb and Smith, 1974; Johnson et al., 2010; Feng, 2011). The organic matter present is thermally immature kerogen, which yields liquid oil upon retorting (Brobst and Tucker, 1973; Mõtlep et al., 2007). Although commonly referred to as “oil shale,” this study demonstrates that the GRF comprises a variety of rock types in the PCB which also include marlstone, siltstone, sandstone and chemical precipitates (Dyni, 2006).

1.1 Lacustrine Environments of Deposition

The isolation of smaller continental basins from the normalizing influence of larger bodies of water makes them susceptible to aerial exposure and climatic changes, and consequentially more extreme fluctuations in water compositions (Eugster, 1980). Wind, temperature, and precipitation are strong influences on lacustrine sedimentation and depositional trends, so that lake basins may experience relatively large variations in water volumes, depths,
currents and basin shape (Eugster, 1980; Last and Ginn, 2005). Size and depth of a lacustrine basin have a great effect on the character and permanence of the depositional environment. Shallower lakes are more likely to exhibit ephemeral, seasonal fluctuations such as playa characteristics and groundwater discharge (Dyni, 1998; Last and Ginn, 2005). Deeper lakes are less likely to be prone to seasonal changes, and are therefore more likely to be perennial. Deposits in deeper basins are less susceptible to the influence of wind on currents and erosion, and may also become immune to seasonal changes which cause turnover of the water column in shallower bodies of water (Drever, 1997). The composition of ground water is a major influence on the ecology and sediment types in a lake, often moreso than fluvial input, especially for those in which drainage is restricted in a closed basin (Eugster, 1980; Last and Ginn, 2005). Common processes which occur in fresh bodies of water in restricted basins include eutrophication, which leads to reducing conditions upon the depletion of oxygen by abundant algal growth (Drever, 1997). When regular turn over and mixing does not occur, reducing conditions may become a permanent chemical state (Drever, 1997; Last and Ginn, 2005). Perennial lakes tend to have quiet, low energy bottom waters where finely laminated sediments deposit and a chemically and thermally stratified water column commonly develops (Smith, 1983; Drever, 1997; Last and Ginn, 2005). Lack of an integrated drainage system can cause evaporation to be a greater influence on the concentrations of solutes that accumulate in closed basins (Drever, 1997; Dyni 1998). Lacustrine systems may have higher rates of evaporation than outflow in dryer climates, which can allow extremes in water chemistry and high salinities to develop. (Eugster, 1980; Bohacs et al., 2000; Last and Ginn, 2005; Tänavsuu-Milkeviciene and Sarg, 2012). Lacustrine depositional environments are therefore conducive to the formation of unusual authigenic minerals (Eugster, 1980; Dyni, 1998; Last and Ginn, 2005).

The GRF of the PCB was deposited during the Eocene in a fresh to saline perennial lake which likely became stratified early in its history (Brobst and Tucker, 1973; Smith, 1983; Johnson et al., 2010; Feng, 2011). The GRF is analogous to other evaporative, saline lacustrine sedimentary sequences of interest including Africa’s Lake Tanganyika and Lake Malawi (Cohen and Thouin, 1987, Lyons, 2009), offshore Brazil’s Espirito Santo and Thailand’s Mae Sot Basin (Boak, 2009; Dyni, 2006). A deep, meromictic lake has been proposed as the most likely model to explain the depositional conditions which produced the GRF, and supported by other studies in research related to this thesis (Desborrough, 1978; Suriamin, 2010; Feng, 2011; Tänavsuu-
Milkeviciene and Sarg, 2012). A stagnant, reducing, lower layer of water was established early in the lake’s development, which became increasingly alkaline and accumulated a very high concentration of salts. A fresher, more oxygenated upper layer of water was able to maintain productive organisms which contributed high quantities of organic matter that descended and were preserved in high proportions in the oxygen-depleted sediments of deeper waters (Bradley and Eugster, 1969; Desborough, 1978; Johnson, 1981). The decay of abundant organic matter in the relatively low-energy, reducing waters of a deep restricted basin, in an increasingly arid climate, allowed for alkalinity and thermal and density stratification to develop, concentrating large quantities of solutes and promoting the formation of rare authigenic minerals (Eugster, 1980).

The GRF serves as an end member example for the depositional environments which can occur in continental restricted basins. Characterization of the variability of mineral concentrations can contribute to the understanding of the conditions required for the formation of economically and industrially important salt and carbonate minerals. The analysis and understanding of mineral distributions in the GRF is key to understanding controls on depositional conditions in these types of extreme environments. Additionally, the findings from this type of comprehensive mineral analysis can be readily transported to other lacustrine sedimentary sequences where saline minerals are commonly precipitated (Cole and Picard, 1978). The extreme conditions pervasive during the deposition of the GRF may have existed in other restricted basin environments to lesser extents and in shorter durations, making the GRF an end member analog that may be extended to many fine-grained, organic-rich facies, including oil and gas – bearing shales.

1.2 Motivations

The mineralogy of the GRF has been studied by scientists for over 75 years, especially in the depositional center where oil shale is richest in organic content. Many papers have been published which address the unusual minerals of the GRF individually, especially those of economic importance (Bradley, 1928; Milton and Fahey, 1960; Smith and Milton, 1966; Tank, 1969; Milton, 1971; Surdam and Parker, 1972; Brobst and Tucker, 1973; Goodwin, 1973; Smith and Robb, 1973; Beard, 1974; Robb and Smith, 1974; Williamson, 1974; Cole and Picard, 1978; Dean et al. 1981; Ratterman and Surdam, 1981; Smith, 1983; Remy and Ferrell, 1989; Dyni,
The work in this thesis attempts to present a comprehensive quantitative mineral dataset for the GRF in the PCB for the common minerals in the assemblage as well as the exotic members. Milton (1956, 1971) was responsible for much of the early work to publish a complete list of minerals identified within the greater GRF basins, which initially identified 33 minerals in 1957, and increased to over 75 minerals in a later paper in 1971 (Milton, 1971). In this thesis over 35 minerals have been identified in the Piceance Basin alone.

As a consequence of the fine-grained nature of the GRF, X-Ray Diffraction (XRD) and microprobe analysis played a key role in the evaluation of mineral composition and therefore the understanding of depositional environment (Brobst and Tucker, 1973; Mason, 2007). The mineralogy of the GRF has been studied by qualitative and semi-quantitative means in several instances (Brobst and Tucker, 1973; Robb and Smith, 1974; Cole and Picard, 1978; Dean et al. 1981; Pittman, 1996; Tuttle, 2009; Suriamin, 2010). Previous studies of mineral assemblages of the GRF were done before the advent of the relatively new technology of quantitative X-Ray diffraction (QXRD) (Omotoso et al., 2006; Środoń et al. 2001; Środoń, 2006; McCarty 2009). Before quantitative XRD analyses were available, data had been restricted to identification and qualitative description of mineralogy (Milton, 1956, 1971; Środoń et al., 2001). Semi-quantitative estimates of mineral percentages first became possible by manual relative peak height estimations. Quantification by peak height estimation was limited by the fact that it was normally too lengthy a process to measure more than one primary peak per mineral. Therefore, variations in secondary reflections could not be addressed in these calculations which introduced error in quantification. In addition, samples containing other minerals with adjacent or overlapping peaks could obscure or interfere with the primary peak (Cole and Picard, 1978). The results of semi-quantitative estimation by peak height can only be confidently applied to relative changes in the quantities of the same mineral from sample to sample, because equal peak heights of two different minerals do not imply equal quantities (Brobst and Tucker, 1973; Robb and Smith, 1974; Środoń et al., 1999)

Many analytical techniques require measurements of a standard reference material in order to normalize the response of an unknown sample to a known quantity. Pure mineral standards are not readily available for many of the rare minerals present in the GRF, and consequently in many studies, protocols used were not able to calibrate instruments for accurate
detection of these minerals (Środoń et al., 2001; Monecke, personal communication, 2010). In addition, the use of internal standards for quantification was not a ubiquitous procedure in the previous century. Sample preparation techniques have now been refined to minimize inherent factors that distort the relative intensities of XRD reflections, such as preferred orientation and homogeneous grain size (Brobst and Tucker, 1973; Środoń et al., 1999). In Brobst and Tucker (1973) experiments were performed to determine what sample preparation and techniques were optimal for improvement of the accuracy of XRD results. Samples were pressed into pellets, rather than packed as loose powder, which introduces error in quantification due to crystal orientation effects. Therefore, this thesis is one of the first studies in the public domain that applies modern quantitative XRD methods to the study of mineralogy in the GRF of the Piceance Basin.

1.3 Objectives

A summary of the objectives of this study are: 1) to construct a record of the stratigraphic variation in mineralogy of the entire GRF in the PCB, and interpret it in the context of the basin history of major lake stages; 2) to quantify the differences in mineralogy across facies from basin center to the basin margin and evaluate the changes in the environments of deposition and subsequent diagenetic alterations; 3) to identify the mineral assemblages present and their significance in terms of the location and conditions at the time of the deposition.

These objectives are addressed by 1) sampling from cores and outcrops that span the entire thickness of the formation, and integrating results with stratigraphic interpretations of lake history from the same cores and outcrops; 2) choosing cores and outcrops that represent the two end member environments of deposition, namely the basin margin and the basin center, and performing petrographic and scanning electron microscopic (SEM) study to evaluate the morphologies of authigenic phases; 3) using quantitative data to: a) describe relationships between minerals, b) compare mineral proportions relative to sampling location, c) define rock types, d) compare mineral concentrations with inorganic chemistry data from the same samples, and e) use geochemical proxies to elucidate conditions during mineral deposition.
1.4 Previous Literature and Significance of this Research

Four major articles have been published since Milton (1971) that documented attempts to evaluate the relative abundances of the major minerals present in the GRF of the PCB in Colorado. All four papers used peak height measurements of XRD patterns to estimate the relative concentrations of a limited suite of seven to twelve major minerals. These key papers were all published in the 1970s and 1980s, and include Brobst and Tucker (1973), Robb and Smith (1974), Cole and Picard (1978), and Dean et al. (1981). Buddingtonite, an ammonium feldspar both common and abundant in the GRF of the PCB, is not represented in any of the four studies, having been first documented in 1964 in igneous rock of a mercury mine, and not in oil shale until 1976 (Loughnan and Roberts, 1983; Taylor et al. 1985; Krohn et al. 1993). In addition, semi-quantitative determination of clay minerals is absent or limited to only illite in these articles.

Providing a vertical mineral profile which covers the full stratigraphic thickness of the GRF in the PCB was a main goal of this study. The research in this thesis presents data from 117 samples from two cores and two outcrop sections, which span the whole GRF. Two of the four previously mentioned publications also documented the entire thickness of the GRF, whereas two evaluated the main Parachute Creek member. Brobst and Tucker (1973) presented XRD data from 650 outcrop samples from the Parachute Creek member. Their study summarized peak height intensities for seven to nine major minerals, and provided detailed descriptions of the measured sections. In Cole and Picard (1978) 198 outcrop samples from the Parachute Creek member in the margin of the Piceance Basin and Uinta Basin were analyzed. Occurrences of six to eight minerals were reported as peak height, and then summarized as abundant, common, or rare and plotted vertically adjacent to the three measured sections from the Parachute Creek member. Their research also included petrographic study to determine the mineral composition of grains versus matrix or cement. Robb and Smith (1974) identified 15 minerals from the Colorado Core Hole No. 1 (CO-1) covering all major zones of the entire formation. Peak height measurements for eight minerals were plotted on a histogram against depth profiles. This study was significant because the profile used very dense sampling, with 1,072 samples over 2,060 ft. of core. A detailed description of the core was also provided along with the oil yield and resistivity log for the same core, allowing for stratigraphic correlation of the samples in Robb
and Smith (1974). Dean et al. (1981) also published a complete stratigraphic profile over the entire formation thickness for twelve minerals. Their research included dense sample spacing with 1500 samples at 0.3 meter spacing from the CR-2 core just north of the PCB center. Optical Emission Spectroscopy (OES) elemental analysis and Fischer Assay oil yield were also included for the same core in this study. In this thesis, gamma ray, oil yields and stratigraphic descriptions from Tänavsuu-Milkeviciene and Sarg (2012), are integrated with the mineral depth profiles allowing for correlation of the formation.

Recognition of stratigraphic transitions present in the mineral assemblages of the GRF in the PCB in two historical datasets represents another motivation for this project. Two transition zones are marked by significant changes in the proportions of most major minerals in both the CR-2 and CO-1 cores reported by Dean et al. (1981), and Robb and Smith (1974), respectively. These transitional zones, made evident by simultaneous shifts on semi-quantitative vertical depth plots, were used as one basis for sample selection in this thesis. A goal of this thesis is to confirm the existence of these zones, and interpret them with the use of a more complete and quantitative mineral set. Therefore, results of this study are compared to the data for the CO-1 and CR-2 cores in these two publications.

Lateral variation in mineral assemblages is interpreted to represent changes in the depositional environment relative to position in the basin. Identifying lateral mineral anisotropy also establishes a link between compositional variation and facies changes. Sampling locations for this research were therefore chosen to represent the two end member facies: the basin margin and the basin center. Two of the previous publications, Cole and Picard (1978) and Brobst and Tucker (1973) also addressed lateral variation in the design of their research. Cole and Picard (1978) looked at relative mineral distributions across basin-margin to open-lacustrine lithofacies of the Parachute Creek Member of the GRF, in both the Piceance Creek and Uinta Basins. In the PCB, they compared relative abundances of nine major minerals in three margin locations, including the Douglas Pass outcrop, with data from the CO-1 core in the basin center from Robb and Smith (1974). Results revealed that carbonate minerals showed zonation from nearshore to offshore lacustrine locations, with iron-rich dolomite being most abundant in basinward locations and calcite more common in marginal locations. Silicate minerals were reported as detrital in origin at the basin margin, and as authigenic or diagenetic in origin in open lacustrine oil shale facies (Cole and Picard, 1978). In Brobst and Tucker (1973) lateral variation was addressed by
sample collection from three outcrop sections of the Parachute Creek member from the West, East and North sides of the PCB. As these samples were collected from outcrop, they only represent basin margin sections. Facies changes were also evaluated with horizontal sampling along two thin oil shale beds, three-four inches thick, every 20 to 100 feet, over hundreds of feet of outcrops. Results showed that the mineral proportions are relatively uniform along the beds in the nearshore depositional environment (Brobst and Tucker, 1973).

Sample rock types have been defined in this thesis by integrating grain size with mineral compositions. Mineral quantification is especially instrumental in evaluating rock types in formations such as the GRF, where there is a predominance of very fine-grained facies. Rock types are categorized in this work according to proportions of the four major classes of minerals present: divalent carbonates, framework silicates, clays, and saline minerals. Rock types identified in this thesis vary according to location in the basin, both by mineral content and grain size. By grain size, rock types in the basin margin include fine sandstone, siltstone, mudstone and chemical precipitates, and in the basin center, include siltstone, mudstone and chemical precipitates. Fine-grained rocks in both basin locations are found to consist of subequal portions of marlstone and siliceous mudstone.

Brobst and Tucker (1973) assessed mineral compositions in context of four major rock types based on an assumed correlation of color with oil content: marlstone, light brown oil shale, medium brown oil shale, and dark brown oil shale. Zeolite mineral contents were found to vary in accordance with these rock colorations. Study of the differences between fine laminations in hand samples also revealed that mineralogy differs between lighter and darker colored beds, as well as between coarser and finer grain sizes (Brobst and Tucker, 1973).

Cole and Picard (1978) also reported their XRD results in reference to the rock types that were sampled. The 1978 study designates samples as being representative of either nearshore rock types: sandstone, siltstone, claystone, algal carbonate, or other carbonate; or open lacustrine rock types: tuff, marlstone, or lean, low, moderate, rich or very rich oil shale. Mineral proportions for six major components are given for each rock type in peak height, or as percentage of total carbonates for the case of calcite and dolomite. Compositions were compared between sandstones from the Mesaverde Group, GRF and Uinta formations. The GRF sandstone had the most quartz and least calcite of the three locations (Cole and Picard, 1978).
Study of mineral components which formed as authigenic or diagenetic phases advances understanding of mineral origins and the conditions that led to their deposition. Sampling in Brobst and Tucker (1973) concentrated on intervals rich in dawsonite and analcime, which are abundant in the GRF of the PCB. These samples were analyzed relative to quantities of co-occurring minerals to test hypotheses about potential mineral replacement relationships. It was found that dawsonite and quartz covaried in quantities, and dawsonite varied inversely with analcime quantities. Analcime was analyzed for Na, Al, and Si to evaluate the ratios of the chemical components in respect to dawsonite. The explanation suggested is that analcime breaks down into quartz and dawsonite under high carbon dioxide concentrations (Brobst and Tucker, 1973).

An advantage to sampling short distinct sections of core for XRD quantification is that a sample is more likely to represent only one set of depositional conditions. XRD samples representing only 1 inch of stratigraphic thickness were used in Brobst and Tucker (1973). Samples homogenized over a larger interval of a foot or more, as used in the other studies in Robb and Smith (1974), and Dean et al. (1981) do not provide fine-scale stratigraphic resolution. In contrast to these studies of the CO-1 and CR-2 cores, samples in this thesis are not averaged over a large interval, but represent a smaller stratigraphic unit of 2 inches. Quantitative analysis will show truer proportions and specific relationships between minerals, and have better correlation with geochemical proxy data. Robb and Smith (1974) evaluated quantitative relationships between different minerals as a means to understanding their stratigraphic distributions. Their study identified sets of mineral associations which occur in separate stratigraphic zones; even though large-interval averaged samples were used. They found that although dawsonite and nahcolite both are most abundant in the saline zone, the two minerals do not occur together in the same sample except in small quantities. In contrast, a positive quantitative relationship for dawsonite was identified in the saline zone with quartz, just as was found in Brobst and Tucker (Robb and Smith, 1974). Mineral relationships are evaluated in this thesis in order to confirm and improve findings by previous researchers by employing a more complete mineral assemblage with quantitative values.
Figure 1.1 Map of the Piceance Creek Basin, Greater Green River Basin, and Uinta Basin showing the boundaries of the Green River Formation Oil Shale. Modified from Johnson, 2010.
CHAPTER 2
GEOLOGICAL SETTING

2.1 The Piceance Basin

The Piceance Basin of Western Colorado (also known as the Piceance Creek Basin or PCB) is part of a larger Eocene sedimentary system that includes the Uinta Basin of northeastern Utah, and the Sand Wash Basin of northwestern Colorado, and Green River, Great Divide, and Washakie Basins of Southwestern Wyoming (collectively the Greater Green River Basin) (Figure 1.1). The Green River Formation (GRF) was deposited across all six basins in three states (Wyoming, Colorado and Utah), which hosted a large lacustrine complex over a period of about 10 Ma (Smith et al., 2008; Johnson et al., 2010). Paleolake Gosuite occupied the northern Greater Green River Basin, and on the other side of the Uinta Mountains, Lake Uinta occupied the Uinta and Piceance Basins to the South (Figures 1.1) (Dyni, 1996; Dubiel, 2003).

These basins began to form during the Laramide Orogeny in the Cretaceous. The continental system developed after the final eastward regression of the Cretaceous Seaway from the area, when marine shale-rich deposits of the Mancos and Mowry Groups gave way to the sandstone and coals of the Mesaverde Formation/Group in the Cretaceous, and the fluvial Wasatch Formation in the Paleocene (Figure 2.1). The Eocene Green River Formation (GRF) sediments deposited in the group of large lakes created from the reactivation of deep faults in the Precambrian basement (Dubiel, 2003; Smith et al., 2008). These fresh to saline lakes were intermittently isolated or in communication when climatic and tectonic changes caused fluctuation in lake water levels (Dyni, 1996; Dubiel, 2003; Johnson et al., 2010; Tänavsuu-Milkevičiene and Sarg, 2012). The GRF began its main deposition in the Piceance Basin about 53 Ma. It was marked by a lakewide transgression known as the Long Point transgression, when two smaller freshwater lakes merged to form the larger Lake Uinta (Johnson 1984; Johnson et al., 2010). This connected the Uinta Basin of northeastern Utah and the Piceance Basin of Western Colorado across the Douglas Creek Arch, a topographic high with low subsidence rates through the Paleocene and Eocene epochs (Figures 1.1, 2.1) (Self et al., 2010). Lake Uinta covered up to 22,000 square miles at its maximum extent (Dyni, 1996). In the Piceance Basin,
which encompasses roughly 6000 square miles, the GRF deposited over roughly 5 Ma (Figure 1.1) (Smith et al., 2008; Johnson et al., 2010).

**Figure 2.1** Stratigraphic diagram of formations of the Piceance and Uinta Basins relative to the Green River Formation in the Cretaceous and Tertiary periods. The Douglas Creek Arch was a topographic high connecting the Piceance to the Uinta Basin during the deposition of the Green River Formation in the early and middle Eocene. S = source rocks, green circles = significant oil production, open circles = significant gas production. Diagonal line fills = hiatus in deposition. Modified from Dubiel (2003).

Early in the depositional history of the GRF, Lake Uinta in the Piceance Basin became a deep, stratified lake. The PCB received outflow from Lake Gosuite to the north, and the Uinta Basin to the west, and had long hydrologically closed periods (Smith et al., 2008; Johnson et al., 2010; Tänavsuu-Milkeviciene and Sarg, 2012). The lake experienced major fluctuations in water depths and was intermittently brackish to hyper-saline and highly alkaline (Bradley and Eugster, 1969; Desborough, 1978; Johnson, 1981; Dyni, 1996; Smith et al., 2008). Evidence of an established meromictic lake includes chemical precipitation of thick beds of saline minerals in the basin center, high rates of organic matter preservation, and fossil fish and ostracods found in
the margins of the basin (Johnson et al., 2010; Self et al., 2010; Tänavsuu-Milkeviciene and Sarg, 2012). The GRF in the Piceance Basin shows distinct lithologic and mineralogic variability from that of the GRF deposited in the Uinta and Greater Green River Basins, and is the richest in oil shale and saline minerals (Smith, 1983; Smith et al., 2008; Johnson et al., 2010). In the mid-Eocene, an influx of fluvial deposits from the North began to enter the Uinta-Piceance Basin, as increased volcanic activity filled Lake Gosuite with sediment in the Greater Green River Basin (Johnson et al., 2010). Subsequently, Lake Uinta was closed in the Piceance Basin, as it was buried under Uinta Formation fluvial sandstone (Dubiel, 2003; Johnson et al., 2010).

2.2 Stratigraphy of the Green River Formation

The GRF is composed of lacustrine and fluvial deposits which intertongue with the fluvial Wasatch Formation below and the fluvial and volcaniclastic Uinta Formation above, shown in figure 2.1 (Johnson et al., 2010). The clastic sediments of the GRF are derived from erosion of the Uinta Mountains, the Uncompahgre Uplift, the White River Uplift, and the Elk Mountains bordering the basin (Figure 2.2) (Dyni, 1996). These uplifts contributed sediment from granite, gneiss, and older sandstone and shale, as well as chemical constituents from Paleozoic limestone. These rocks, in addition to volcaniclastic sediments from the Absaroka volcanic field of Wyoming, were sources of felsic and mafic silicate and clay minerals, which served as precursors to the variety of authigenic minerals found in the Piceance Basin (Smith, 1983; Mason, 2007; Smith et al., 2008; Johnson et al., 2010). The basin margin is richer is sandstone, siltstone, clay mineral-rich mudstone, and limestone. The basin center contains less siliciclastic sediment of coarser grain sizes, with higher organic matter content, thicker and more abundant oil shale mudstone and subaqueous evaporite beds, and is richer in dolomitic micritic marlstone (Dyni, 1996; Johnson et al., 2010).

The thickness of the GRF in the Piceance Basin is about 3000 feet near the center of the basin, and about 700 ft thick at the basin margin at the Douglas Pass outcrop (Johnson et al., 2010; Tänavsuu-Milkeviciene and Sarg, 2012). The generalized stratigraphic column for the GRF includes two main members in the center of the basin, the Garden Gulch illitic oil shale at the base, and the Parachute Creek feldspathic/dolomitic oil shale above it. The sandstone and carbonate rich Douglas Creek member is found in the southwestern part of the basin (Suriamin, 2010; Johnson et al., 2010). The Douglas Pass basin margin outcrop includes the Douglas Creek
member and Parachute Creek member. In the eastern part of the basin, the members include the Anvil Point and the Cow Ridge. (Figure 2.3) (Suriamin, 2010; Johnson et al., 2010; Tänavsuu-Milkeviciene and Sarg, 2012).

Figure 2.2 Map of the Piceance Basin and depositional extent of the Green River Formation. Black contour lines indicate the main area of saline mineral deposition, showing isopach thickness of nahcolitic oil shale of 500 and 100 ft. Inner light blue zone is the area of bedded halite deposition. Locations of the Uncompahgre Uplift, White River Uplift and Uinta Mountains are indicated. Study sections were chosen to represent two end members in depositional environment of the paleolake: the deepest basin center, where the most extensive deposition of saline minerals occurred; and the nearshore basin margin, where detrital facies are most abundant. Locations of wells and outcrops sampled are shown relative to the main saline depositional area and for three wells from which comparison data has been used in this study: CR-2, CO-1, and the USBM 01-A. Sections representing the basin center are the Wolf Ridge Minerals John Savage 24-1, Shell 23X-2 cores, and the CR-2 and CO-1 cores. Sections representing the basin margin in two outcrop areas at the Douglas Pass, which are located on the Douglas Creek Arch. Modified from Dyni, 1996 and Tänavsuu-Milkeviciene and Sarg, (2012).
Fischer assay oil yields have traditionally been used for defining alternating oil-rich (R) and oil-lean (L) oil shale zones in the GRF, representing changes in productivity and preservation of organic matter. Rich and lean zones are extraordinarily laterally continuous, approximately chronostratigraphic strata, many of which are correlative across both the Uinta and Piceance Basins (Smith, 1983; Johnson et al., 2010). These rich and lean zones number from 15-17 in total in the PCB, and start at the base at Rich Zone 0, or R0, and terminate at the top of the Parachute Creek member with R8 (Figures 2.3, 2.4) (Dyni, 2008; Johnson et al., 2010; Tänavsuu-Milkeviciene and Sarg, 2012). Rich and lean zones L0, R0 and L1 are clay-mineral rich and are included in the Garden Gulch member. Rich and lean zones R2 through R8 are dolomite and feldspar rich and included in the Parachute Creek member. Rich zone R8 may be part of the Uinta Formation in some sections where it intertongues with the upper GRF. Rich zone R7 is commonly referred to as the Mahogany zone, and is one of the most oil shale-rich zones, and the most pervasive unit in the basin. It is a 60-200 ft interval of the Parachute Creek member targeted for. and Sarg (2012) are used here. Johnson (1985), and Johnson et al. (2010) originally subdivided the sediments of the GRF into five stages, representative of time-stratigraphic periods in lake history. Tänavsuu-Milkeviciene and Sarg, 2012, have since updated the evolutionary stages of Lake Uinta, using facies association distributions, gamma ray markers and Fischer Assay oil shale richness to divide the stratigraphic column into six separate lake stages. The six lake stages correlate with rich and lean zones and reflect the changes in depositional environment and large-scale sedimentological trends of the GRF (Figures 2.3 and 2.4). The six lake stages, starting from the base of the GRF, begin with S1, the fresh to brackish lake stage, which includes rich and lean oil shale zones R0, L0, R1 and L1. The next lake stage, S2, is the transitional lake stage, during which lake Uinta in the Piceance Basin experienced high siliciclastic input in a more arid climate, and began the first saline mineral deposition, including zones R2, L2, and R3. The third lake stage, S3, is the highly fluctuating lake stage, including R4, L4, R5, and L5, during which rapid changes in water levels, and the greatest deposition of saline minerals occurred. Lake stage S4, the rising lake stage, includes R6 and L6 (also known as the B Groove), during which there was increased input of freshwater into the basin. Lake stage S5, the high lake stage, includes the Mahogany Zone which coincides with rich zone R7, during which stable lake levels deposited deep-water, laminated facies with rich, pervasive oil shale. Finally, S6 the closing lake stage, completes the sequence with L7 (also known as the A Groove), and
R8, when increased siliciclastic input began to fill the basin (Tänavsuu-Milkeviciene and Sarg, 2012).

The lower approximately one quarter of the GRF stratigraphic column is composed of illitic oil shale (mudstone and marlstone) of the Garden Gulch Member, which is encompassed by lake stage S1, and the base of S2. The Garden Gulch Member was deposited in a semi-restricted, fresh to brackish water lake, and contains abundant fish fossils (Figure 2.3).

**Figure 2.3** Stratigraphic column of the Green River Formation members, rich and lean zones, and six lake stages defined by Tänavsuu-Milkeviciene and Sarg (2012) in the Piceance Basin. The Wasatch formation occurs below and Uinta Formation occurs above the GRF. The saline interval indicates the general range of deposition for saline minerals, and the upper and lower salts are the general positions of the thickest halite beds. Modified from Tänavsuu-Milkeviciene and Sarg (2012).
The Parachute Creek member is clay-poor, and comprises roughly the upper three fourths of the GRF. Prior literature has described the Garden Gulch and Parachute Creek members as clay-rich and carbonate-rich respectively, but this thesis has shown that both members are carbonate rich, and the Parachute Creek member is better distinguished as feldspar-rich. Much of the Parachute Creek Member was deposited in balance-filled to closed-lake conditions which allowed for concentration and precipitation of saline minerals. The Parachute Creek includes the rich and lean oil shale zones R2 through R8 in the PCB, including the richest oil shale intervals, especially R4. The Parachute Creek contains the interval of the greatest deposition of saline minerals, the saline zone, which overlaps the majority of lake stages S2 and S3, and can be over 1000 feet thick in the most central part of the basin (Daub et al., 1985; Dyni 2006; Johnson et al., 2010; Self et al., 2010; Tänavsuu-Milkeviciene and Sarg, 2012). The saline zone contains several thick beds of nahcolite and halite, each of which may be over 90 feet thick. Deposition of bedded saline minerals was restricted to the deepest parts of the basin center, whereas nahcolite nodules and small crystals have been identified farther out from the main evaporite depocenter area (Figure 2.2). Halite had the most restricted area of deposition, followed by nahcolite, whereas dawsonite had the widest depositional area (Daub et al., 1985; Dyni, 1996; Dyni, 2006; Johnson et al., 2010; Tänavsuu-Milkeviciene and Sarg, 2012). Extensive leaching is manifested throughout most of the upper stratigraphic units of the Parachute Creek member above the saline zone, including in the Mahogany. Evidence of the dissolution of water-soluble minerals, mainly nahcolite, include collapse breccias, solution cavities, and vuggy porosity (Daub et al., 1985; Pitman, 1996; Dyni, 1996 and 2006; Johnson et al., 2010).

Outlines of the saline depositional areas for nahcolite and halite are delineated on the map of the Piceance Basin in figure 2.2, with isopach contours of the nahcolitic oil shale intervals (Dyni, 1996; Tänavsuu-Milkeviciene and Sarg (2012). Locations of cores, outcrops and datasets used in this study relative to the main saline deposition zones are also denoted in the map. The extent and distribution of nahcolite and halite beds of the subaqueous evaporite facies association can also be seen in the cross-section by Tänavsuu-Milkeviciene and Sarg (2012) in Figure 2.4. The general stratigraphy of the GRF of the PCB from marginal areas through the basin center, and the relationship to the six lake stages is illustrated in the cross-section. The figure also defines the 17 rich and lean zones, 13 sequence boundaries, and roughly 12 of the facies associations defined by Tänavsuu-Milkeviciene and Sarg (2012). Profundal facies associations
dominate in the basin center sections, such as laminated and brecciated oil shale and siliciclastic turbidites. Littoral and sublittoral facies associations dominate in the basin margin sections, such as shoreline and deltaic mudstone and sandstone, microbial carbonate and carbonate shoals, and other oil shale and siliciclastics (Tänavsuu-Milkevičiene and Sarg, 2012).
Figure 2.4 Cross Section of the Green River Formation in the Piceance Basin including five sections used in this study: the basin center John Savage 24-1, Shell 23X-2, and Colorado-1 (CO-1) cores, and the basin margin Douglas Pass outcrops. Lake stages, rich and lean zones, and facies associations are indicated. Cross Section reference location map on the right. A larger version of this figure may be found in Supplemental File Q. After Tänavsuu-Milkeviciene, K., Sarg, J.F., and Bartov, Y. (2013).
CHAPTER 3

METHODS, DATASETS AND DATA QUALITY

The four sections sampled in this study overlap or combine respectively to cover most of the entire thickness of the Green River Formation (GRF) in two general basin locations. Sections were chosen to represent two end members in depositional environment of the paleolake: the basin center, and the basin margin. Sections include two USGS cores representing the basin center facies, richest in oil shale and saline mineral sequences; and two outcrop sections representing the leaner, more siliciclastic-rich, basin margin facies. Photos of core and outcrop samples may be found in Supplemental Files H, I and J.

3.1 Sample Selection and Locations

A subset of 82 samples was selected for this study from a total of 238 samples available from four Piceance Basin sections. Core sections are a record of the deep water column of the center of the ancient lake (thickest formation column). Outcrop sections record the shallower near-shore water depths (shorter stratigraphic column) where lacustrine and fluvial deposits are most likely to reflect changes in lake levels and climatic conditions. Sections representing the basin center are the Wolf Ridge Minerals Savage 24-1, hereafter referred to as the John Savage 24-1, and Shell 23X-2 cores. Sections representing the basin margin include two outcrops at Douglas Pass, which is located on the Douglas Creek Arch. The outcrops are located on the Western margin of the basin, where during high water levels ancient Lake Uinta is proposed to have connected the Piceance Basin to the Uinta basin (Smith et al., 2008). Data from the USGS CR-2, USGS CO-1, and USBM 01-A cores, near the basin center, are also used as comparison datasets. Locations of outcrops and cores are shown in Figure 2.2. Cross sections of each core and outcrop used in this study (except the CR-2) and their relative basinal locations are illustrated in Figure 2.4 constructed by Tänavsuu-Milkeviciene and Sarg (2012).

Cores and outcrops were sampled from depths at which major changes in lithofacies occurred according to stratigraphic descriptions by Tänavsuu-Milkeviciene and Sarg (2012). Samples taken from outcrops at the basin margin did not include the nearly pure limestone carbonate beds for this research project. Carbonate facies of the basin margin section in this
project are described in Suriamin (2010). Samples taken from cores from the basin center did not include the nearly pure halite facies. Facies are shown in the stratigraphic sections described in Figures 3.2, 3.3 and 3.4. X-Ray diffraction (XRD) samples were also selected for optimal stratigraphic depth coverage, to represent each rich and lean zone, lake stage, and rock type present (other than limestone beds or halite intervals), and to correspond with samples which had already been chosen for other analyses such as thin sections. A greater sample density was concentrated at two stratigraphic intervals where prior literature determined that a shift in mineralogy occurs. Intervals of denser sample analyses include the lower transition zone in rich zone R2, where quantities of illite dramatically decrease; and the upper transition zone in rich zone R5, where saline mineral deposition decreases (Dean et al 1981). Rock types of the samples chosen for this study are listed in Supplemental File N.

Twenty-eight samples were chosen from 75 outcrop samples available from the Douglas Pass basin margin sections on Douglas Creek Arch. From the basin center, 39 samples were chosen from 117 core samples available from the USGS John Savage 24-1 core, and 15 of 46 total samples were chosen from the Shell 23X-2 core. The John Savage 24-1 core covers 1503 ft in thickness from depths between 1293 ft to 2796 ft (458.1 m total, from 394.1 to 852.2 m), and is located in the NE quarter of the NE quarter of section 24, Township 1 South, Range 98 West (NE NE Sec. 24, T01S R98W). The Shell 23X-2 core is located NE SW sec. 2, T02S, R98W and covers 528.25 ft sampled from depths of 2165.08 ft to 2693.33 ft.

The two Douglas Pass outcrop sections cover 984 ft (approx. 300 m) and are located along Highway 139. Sample locations from the upper Douglas Pass section are labeled by stations J,K and L (from 39°38'4.44"N latitude, 108°45'47.34"W longitude to 39°38'6.06"N latitude to 108°45'49.02"W longitude), and sample locations from the lower Douglas Pass section are labeled by stations A – I (from 39°35'54.06"N latitude, 108°49'3.00"W longitude, to 39°35'49.44"N latitude, 108°48'22.14"W longitude), and stations M – S (from 39°35'56.28"N latitude, 108°48'12.78"W longitude to 39°36'18.12"N latitude, 108°46'32.34"W longitude).

Eighty-two samples in total were processed and analyzed in the Chevron Energy Technology Company (ETC) X-ray diffraction (XRD) lab in Houston, Texas, using proprietary methods and software. In total, data from 117 samples were used in the mineralogy study, with the addition of XRD data for 35 samples previously analyzed from the same Shell 23X-2 core by ExxonMobil, available through the USGS Core Research Center, in Denver, Colorado. The 46
Shell 23X-2 samples taken were selected to enhance stratigraphic coverage by integrating with the depths of the data for the 35 ExxonMobil samples. A total of 50 Shell 23X-2 samples were used for interpretation. In summary, the basin center is represented by 89 samples (54 Chevron-analyzed and 35 ExxonMobil-analyzed) and the basin margin by 28 samples (Table 3.1). Photos of core may be found at: U. S. Geological Survey Core Research Center (2012) Core Library Number C042 (http://my.usgs.gov/crcwc/core/report/10109).

**Table 3.1** Number of samples from each core and outcrop from the two basin locations, and source of data and methods. Exxon USGS data refers to ExxonMobil analyzed data obtained through the USGS.

<table>
<thead>
<tr>
<th>Sample Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Basin Center Samples</strong></td>
</tr>
<tr>
<td>89</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>35</td>
</tr>
<tr>
<td><strong>Basin Margin Samples</strong></td>
</tr>
<tr>
<td>28</td>
</tr>
<tr>
<td>22</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
<tr>
<td>117</td>
</tr>
</tbody>
</table>

### 3.2 Sample Preparation

Special care was taken to avoid water in sample processing for all analyses, especially in thin section preparation, in order to preserve water-soluble evaporite/saline minerals.

Each of the 82 core samples taken for analysis at Chevron, was approximately 2 by 2 by 5 cm, from 10 cm diameter cores. Seventeen of 39 John Savage 24-1 core pieces, and all 15 Shell 23X-2 core samples were alternately hand crushed and sieved using a ceramic mortar and pestle and with only impact forces (percussion as opposed to shearing), until all material passed through a 40-mesh screen (to 0.4 mm) as per Chevron XRD protocol. The remaining 22 John Savage 24-1 samples were taken from pulverized material that had been ball-milled in steel chambers with steel ball bearings and/or in a shatter box. Shearing effects may be present in the 22 John Savage 24-1 samples due to extended mechanical crushing times without intermittent sieving. Clay minerals are the softest and most affected by shearing forces, but quantities of clay minerals are low in the John Savage 24-1 set, so effects were expected to be minimal. However, resulting John Savage 24-1 XRD diffraction patterns did show some broadening and shortening of peaks as a result of sample processing. The effect on the quality of mineral identification and
quantification were not considered to be significant for the purpose of bulk analysis of major phases. Supplemental File F shows XRD patterns of ballmilled samples before and after being McCrone milled.

All 28 Douglas Pass outcrop samples were homogenized from boulder size by hand with a hammer, and then jaw crushed to coarse gravel. The gravel-sized material was mixed and divided into aliquots representative of the entire hand sample using a large riffle splitter at the US Geological Survey Central Minerals and Environmental Resources Science Center in Denver, Colorado. Douglas Pass samples chosen for XRD were then further divided using an 8-jar rotary splitter into smaller aliquots (approx. 20 g) at the Chevron ETC lab. Due to the large variability in outcrop rock types, Douglas Pass samples required several different sample preparation methods to achieve the 0.4 mm grain size. Selected fine-grained Douglas Pass samples, with assumed high clay mineral contents, were processed in the same manner as core samples by hand crushing with a ceramic mortar and pestle and sieving to 40-mesh. Most well-cemented Douglas Pass samples of sandstone or siltstone rock types were alternately sieved and mechanically ground for less than 10 seconds at a time using an automatic mortar and pestle, until all material passed a 40 mesh screen.

Once all samples were homogenized and reduced to less than 0.4 mm grain size, they were then divided using a small riffle splitter into 2 and 3 g aliquots for XRD and chemical analysis respectively. This ensured that the same exact material was used for both analyses, and results from each would be quantitatively equivalent and comparable. Zinc oxide was added at 10% by weight as an internal standard to the 3g aliquot for XRD analysis. Internal standard addition during sample preparation was a source of error for quantification because samples evaluated by JADE showed that actual zincite amounts were commonly higher than 10 wt%, up to 14 wt %. Error in quantification by JADE may account for some deviation from 10 wt%, but all three samples analyzed for zincite erred on the high side. Supplemental File F shows XRD patterns for samples with and without added ZnO internal standard. Secondary zincite peaks, at 45.45 and 56.48 2-theta, can obscure identification of halite, therefore many samples were scanned with and without the internal standard. It was determined halite is still identifiable as a shoulder on the zincite peak when the internal standard is present.

The 3g XRD aliquot with internal standard was then wet-ground for 5 minutes with hexane in a McCrone Mill using plastic chambers with agate beads. Milling produces a narrow
particle size distribution to less than approximately 20 microns, to ensure XRD peak intensities will be representative of mineral proportions (Omotoso et al., 2006). The 22 John Savage 24-1 samples from ball-milled material were McCrone milled for a much shorter time period, up to 2 minutes, just long enough to homogenize the grain sizes and mix in the internal standard, in order to avoid worsening of any shearing effects present. XRD spectra of ball-milled material before and after McCrone milling are shown in Supplemental File F.

Each dried sample was gently re-homogenized with a spatula by hand after evaporation of the organic solvent. Samples were loosely packed into side-loading XRD mounts against frosted plastic to minimize crystal orientation effects from compaction. Various materials used in the crushing and homogenization of samples have potential for introducing trace levels of contamination which do not affect bulk mineralogic results, but may change the trace element chemical analysis. Specifically, the use of crushing beads composed of agate (as opposed to harder zirconium material) in the McCrone Mill, will add small amounts of impurities known to be included in quartz.

3.3 Analytical Methods and Instrumentation

All 82 samples were characterized by XRD for bulk mineralogy at Chevron ETC based on methods of quantitative analysis by Średoń et al (1999) and (2001) and described in Omotoso et al. (2006). Samples were analyzed using a Thermo XTRA diffractometer with a θ-θ goniometer and 250 mm radius, equipped with a solid-state Si detector. Diffractometer operation settings were 40 kV and 40 mA total power. Scan parameters were 2 seconds per step, with a 0.02 step size, from 5 to 65 degrees 2-theta, using CuKα radiation transmitted through a 1.00 mm divergence and 1.80 mm antiscatter slit. Detector slits were 2.00 and 0.3 mm. XRD patterns were collected using side-loading sample mounts with a10 wt% internal standard of commercially obtained ZnO powder mixed in with the sample. Resulting patterns were corrected for lateral shifts by aligning the spectra with the primary quartz peak at 26.6 2-theta, and primary zincite peak at 31.8 2-theta. Supplemental Files E, F, and G contain raw XRD patterns for all samples analyzed at Chevron ETC.

Chemical analysis was also performed for all 82 XRD samples, by Activation Laboratories Ltd in Ontario, Canada. Major elements were analyzed by lithium metaborate/tetraborate fusion inductively coupled plasma whole rock fusion (ICP - WRA), and trace
elements by fusion mass spectrometry (ICP-MS). Sulfur was analyzed by ICP, organic carbon (Corg) by infrared spectroscopy, and total carbon (CO$_2$) by coulometry. Detection limits and Activation Laboratories Ltd method specifications are listed in Supplemental File D with tables of the results of chemical analysis.

Samples with significant clay mineral contents were analyzed for cation exchange capacity (CEC), at Chevron ETC, to determine the proportion of expandable smectite by spectrophotometric absorbance. CEC procedures were modeled after Bardon (1993), using hexammine cobalt (III) chloride. Chemistry and CEC analyses were performed on splits from the same approx. 15-20 gram sample powder as used for quantitative XRD mineralogy. Cut-offs for clay type determinations are defined as greater than 55 meq/100g for smectitic samples, and less than 20 meq/100g for illitic samples. The error for CEC analysis is 2 meq/100g, according to Chevron ETC methods (Bardon et al. 1993).

Samples must contain at least 3 wt% 2:1 layer clay minerals for CEC analysis to be applicable. If clay mineral contents are below this, the relative error of the quantification is elevated, and the calculated result for the CEC measurement is given as “not determinable” (ND). Based on quick initial pattern interpretations to determine rough total clay mineral contents, 52 out of 82 XRD samples were selected for CEC analysis. These included all 28 Douglas Pass samples, nine of the 15 Shell 23X-2 XRD samples, and 15 of the 39 John Savage 24-1 samples. Four of the 52 chosen samples gave results as ND, being determined by CEC to have below the minimum clay mineral content required for calculations. These four samples included Douglas Pass 106JK (830 ft., stage S5, 3.0 wt%), John Savage 24-1 JS-57 and JS-73 (2204 and 2031 ft., both in stage S3), and Shell-26 (2467.7 ft, stage S2). Subsequent higher quality pattern interpretation indicated that 3 additional samples in Stages 2 and 3 of the basin center, did contain over 3 wt% clay minerals, and should have also had CEC analysis. These samples included John Savage 24-1 JS-68, JS-28, and JS-3, with total clay mineral contents of 7.3, 7.9, and 5.5 wt% respectively. Supplemental File K contains the complete table of CEC results.

Thin sections were made from twenty selected samples from the Douglas Pass margin section, and four samples from the John Savage 24-1 basin center core. No thin sections were made from the Shell 23X-2 lower basin center section. Twelve of the twenty Douglas Pass samples selected for thin sections were analyzed by XRD. Thin section optical microscopy is a
method of limited value with the extremely fine-grained textures of most GRF facies, and many of the major mineral phases of interest have nearly identical optical properties. Therefore, only a cursory review of available thin sections was conducted by optical microscopy to find grains and textures of interest, which were then taken to the SEM to verify the compositions. The four basin center John Savage 24-1 samples (Figure 3.1) were analyzed by scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS) at the Colorado School of Mines. The selected thin sections were polished and sputter coated with gold in preparation for SEM-EDS. The instrument used was a JEOL 840A equipped with a Princeton Gamma Tech Avalon EDS system, run at 20 kV accelerating voltage.

**Figure 3.1** Four basin center thin sections chosen to be analyzed by SEM-EDS, showing the fine grained texture of the mudstone and saline evaporite rock types used for authigenic mineral identification. John Savage 24-1 samples from left to right: JS-35, mudstone, JS-45, subaqueous evaporite, JS-53, subaqueous evaporite, and JS-71, mudstone.

The beam voltage was lowered to 10 kV for samples containing saline minerals such as nahcolite, in an unsuccessful attempt to obtain an EDS spectrum of minerals containing elements that are less stable under the electron beam. Low atomic number elements have low count rates due to high absorption of low-energy K\(\alpha\) x-rays. Therefore the instrument used does not detect carbon, nitrogen, or oxygen; and sodium peaks are substantially reduced in all samples analyzed. For higher atomic number elements, relative EDS peak heights were used to help distinguish between minerals with the same set of elements in the chemical formula (e.g. Al:Si is 1:3 for feldspars, and 1:2-3 for analcime). Magnesium, aluminum and silica peaks may also have minor
attenuations, but any observed effects were not significant for the purposes of this thesis. For instance, reduction in aluminum EDS peaks caused Al:Si ratios in feldspar to be closer to 1:4 rather than 1:3 in some samples. (Krohn et al. 1993; Ramseyer, 1993; Skok, personal communication, 2013).

3.4 Software and Data Interpretation

Sample XRD patterns were interpreted using proprietary Chevron quantification software, which uses comparisons to XRD spectra produced from known standard minerals. Concentrations are reported in weight percent (wt %), and zero values indicate that the phase was not detected. Concentrations which are reported as decimal values (in trace quantities) do not imply that precision is greater than indicated by errors reported in Środoń et al. (2001). Chevron ETC reports state that “… mineral identification was based on correspondence of experimental d-values with the diagnostic hkl reflections from the International Centre for Diffraction Data (1993), (ICDD) reference file and/or other published works,” (Środoń et al. 1999). Further analysis was performed using the software JADE at the US Geological Survey, for two samples (JS-45 and JS-78) which had low quantification totals and anomalous XRD patterns. JADE was able to identify and quantify rare minerals for which standards were not loaded in Chevron’s software. Three additional stratigraphically adjacent samples (JS-71, JS-76, and JS-43) were also analyzed with JADE to check whether significant amounts of the newly identified minerals were present (kutnohorite, natrite, woodhouseite, and northupite), and to cross check with quantification done with Chevron’s software. Only JS-71 contained any of the four newly identified minerals, at less than 2 wt% each, so no further samples were tested. Therefore, trace levels of these minerals are potentially present in additional basin center samples, but are not relevant to bulk analysis purposes. JADE analysis also identified high levels of muscovite in sample JS-71, and a minor amount in sample JS-78. Muscovite is not reported independently from Di 2:1 clay minerals by Chevron’s software, and therefore for the purposes of interpretations, muscovite quantities identified with JADE were reintegrated with illite/smectite. Shell 23X-2 core samples were not tested with JADE for any additional minerals because quantification totals in Chevron’s software were satisfactory. Also the stratigraphic intervals of John Savage 24-1 samples with anomalous patterns are not shared by any Shell 23X-2 samples used in this study. JADE cannot quantify clay minerals or organic matter, so results from
Chevron’s software and JADE analyses were integrated for the five samples to include the newly identified minerals with organic matter and clay minerals. Major mineral quantities in all five samples had good agreement between the two analyses by both software programs, once samples were normalized for OM and clay mineral quantities. Dolomite - ankerite series minerals are also determined differently by the two programs, so dolomite, ankerite and excess-calcium-dolomite were integrated into one category for mineralogy interpretation. Raw XRD patterns for all samples are included in Appendices E, F, and G.

XRD result tables are in Supplemental File A for basin margin Douglas Pass sample sets; and tables of XRD reports by Chevron ETC analysis, JADE analysis, and ExxonMobil data for the Shell 23X-2 well are included in Supplemental File B for basin center datasets John Savage 24-1, and Shell 23X-2.

3.5 Data Quality

Minerals which are members of solid solutions and/or which have less well-crystallized structures, such as clay minerals, and amorphous phases such as organic matter, have higher uncertainty due to broader, less well-defined peaks. Quantification error is larger for XRD peaks which shift position due to ion substitutions, because of increased difficulty matching standards to variable compositions. The amount of error decreases for minerals with well-crystallized structures such as quartz, which display sharp, well-defined peaks in XRD patterns. The greater the concentration of a mineral, the lower the relative error for that quantity (Środoń et al, 2001).

Clay mineral results also have higher uncertainty in this dataset because values were determined from bulk analysis rather than by detailed clay fraction analysis which requires further sample preparation to separate the finer particles from the bulk minerals and a separate XRD scan. Clay mineral reflections occur in the section of XRD spectra below 19° 2-theta, where there is high background in bulk scans. Therefore clay minerals are difficult to quantify without secondary clay-sized fraction sample preparation procedures and detailed separate XRD scans of that spectral region. Pattern matching using a selection of clay mineral standards provided in Chevron’s software gave a rough estimate of clay mineral composition in the bulk analysis performed with this sample set. Therefore, significant uncertainty in clay mineral identification and quantification arises from the methods used for this study from sample preparation, from XRD scanning protocols, and data interpretation. A multitude of standards
were employed in Chevron’s software for interpretation of the solid solution series muscovite-illite-smectite in sample spectra for Reitveld analysis, but these end members are all included in one grouping under Di :1 Clays for report purposes. Chevron’s software reports clay minerals in the following categorizations for bulk XRD analysis: Di 2:1 Clay = dioctahedral 2:1 layer clay minerals: illite, mixed-layer illite-smectite, smectite, and possibly mica; Tri 2:1 Clay = trioctahedral 2:1 layer clay minerals: biotite, phlogopite, biotite/vermiculite, trioctahedral smectites; Tri 1:1 Clay = trioctahedral 1:1 layer clay minerals: serpentine-type minerals and berthierine.

Organic matter is also quantified by XRD analysis with this sample set, with a high uncertainty due to the broad undefined peak exhibited by amorphous matter. Organic geochemical analysis of the same sample set used in this study is described in Feng (2011), which is the source of total organic carbon (TOC) data by Source Rock Analysis (SRA). Organic matter (OM) by XRD was compared to TOC obtained by SRA with good correlations ($R^2 = 0.84$) for the John Savage 24-1 sample set, and the Shell 23X-2 sample set ($R^2 = 0.95$). Correlation between OM by XRD and TOC by SRA for the Douglas Pass sample set had a weaker correlation ($R^2 = .68$). The weaker correlation may be explained by organic matter being present in the basin margin at lower concentrations than in the basin center, and therefore the sample OM peak is more difficult to distinguish from high background in XRD spectra. Organic carbon (Corg), from the chemical analysis by infrared spectroscopy (IR), was plotted against both TOC by SRA and OM by XRD to test which dataset contains the largest error. Results show that XRD analysis has the largest error as the correlation between Corg and TOC was very good ($R^2 = .99$), and the correlation between Corg and OM by XRD is much lower ($R^2 = .70$).

Interpretation of the quantity of organic matter present by XRD is also affected by the presence of buddingtonite or dawsonite in samples, due to overlap of the primary peaks in the area of the spectra in which OM raises the background.

Minerals that are members of solid solution series are reported in lumped categories due to limitations in the detection of individual phases and to reduce uncertainties in interpretation. The feldspars are an example. Chevron’s software allows for individual selection of many different feldspar standards during interpretation for Reitveld analysis, and the raw data for individual samples distinguishes amongst end members, but reports final results in only two categories (KSpar and Plagioclase) for the sample sets. Albite, an important component of the
GRF assemblage, is included with plagioclase without a separate breakout. Additional complications are presented by the fact that Chevron’s software and the program JADE group and identify these phases in different ways. To resolve these discrepancies, and not allow precision to be misleading, the format used in the report generated by Chevron’s software was generally followed for all integrated samples. In order to integrate results generated by Chevron’s software, by JADE, and ExxonMobil Shell 23X-2 data, mineral categories were further generalized where required.

Results for ankerite and dolomite were combined into one category along with excess calcium dolomite in order to reduce uncertainty. Although it is quite certain that high quantities of iron-rich carbonate phases are present in the GRF, including ankerite, interpretation methods could not quantify ankerite as a separate phase from dolomite with sufficient precision. Multiple standards for ankerite and dolomite were available in the Chevron software database. Therefore, for interpretation purposes, two patterns with the most separation as distinct end members were applied for all samples for Reitvelt analysis, which may have had the result of artificially increasing the proportion of ankerite. Further evaluation would be required to define the average iron content of dolomite-series minerals in these samples.

Due to the rare nature of many of the minerals found in the GRF, it is difficult to construct perfect XRD pattern fits during interpretation, due to the lack of multiple standards to choose from in the databases. This was one source of uncertainty in this dataset for buddingtonite, dawsonite and nahcolite due to the availability of only one standard each in Chevron’s software database. Buddingtonite in sample spectra consistently displayed a primary peak shifted by less than 1 degree 2theta left from the standard buddingtonite spectra. Buddingtonite has a very diagnostic peak at 20.5 degrees 2-theta, and the shift observed may be explained by a difference in the calibration of the original scan of the standard, or by a peak shift caused by a substitution, such as a solid solution between buddingtonite and alkali feldspars. Also, the quality of the quantification of buddingtonite was affected in some samples by the presence of other alkaline feldspars with overlapping peaks, especially when combined with smaller quantities of buddingtonite (Krohn et al., 1993; Oh, et al., 1993).

The nahcolite standard also had missing peaks in the spectra which were present in all samples containing nahcolite at 55.3, 58.4, 60.8 degrees 2-theta. A standard pattern was obtained with JADE from the International Centre for Diffraction Data® (ICDD®) database for
comparison, which did show these missing peaks for nahcolite, indicating that the nahcolite standard used in Chevron’s software may not have been scanned out to the full 65 degrees. Nahcolite also breaks down during scanning so that standard spectra have to be artificially touched up to remove peaks from the breakdown product and resulting higher background. Therefore a lower Reitveld fit was attributed to the missing peaks in samples containing significant amounts of nahcolite (McCarty, personal communication, 2011).

Comparison to mineralogy data for the USGS corehole CR-2 from Dean et al. (1981) is complicated by the fact that mineral categories are reported differently than the datasets generated by this study. Albite and potassium feldspars are reported separately, but not plagioclase, and dolomite and siderite are reported, but not ankerite. Buddingtonite was not identified. All minerals quantifications were estimated from measurements of relative peak heights. Therefore, the data may not be used in a direct comparison between minerals, or to other datasets, but only as amounts of one mineral relative to itself as a function of depth (Dean et al. 1981). Consequently, a quantitative comparison of CR-2 mineralogy to results from this thesis is not possible, but a qualitative comparison may be made. Original CR-2 data that were digitized for the purposes of this project are given in Supplemental File C.
Figure 3.2 Sample locations in the upper basin center John Savage 24-1 core stratigraphic section. Oil yield by Fischer Assay in gallons per ton, rich/lean zones, lake stages, formation members and sequence boundaries in the left column.
Figure 3.3 Stratigraphic column and sample depths in the lower basin center Shell 23X-2 core, modified from Tänavsuu-Milkeviciene and Sarg (2012). Samples labeled “Shell-Exxon” were analyzed at the ExxonMobil laboratories from material obtained from the USGS, and samples labeled “Shell-COSTAR” were taken from the same core at the USGS by the COSTAR consortium, and analyzed at the Chevron-ETC laboratories. Oil yield by Fischer Assay in gallons per ton and gamma ray log shown on the left, with rich/lean zones, lake stages, formation members and sequence boundaries.
Figure 3.4 Stratigraphic column with sample depths indicated in the basin margin Douglas Pass outcrop sections, with rich/lean zones, lake stages, formation members and sequence boundaries on the left. Modified from Tänavsuu-Milkeviciene and Sarg (2012).
CHAPTER 4
RESULTS

A diverse set of minerals has been quantified from the Green River Formation (GRF) of the Piceance Creek Basin (PCB) from samples representing two basin locations. The distribution of mineral assemblages in the basin margin and the basin center locations are presented here, as well as the stratigraphic evolution of Lake Uinta. Minerals that occur in abundance in the basin margin include the common rock forming minerals quartz, plagioclase and potassium feldspar, illite and smectite, calcite and iron-bearing dolomite; as well the less common zeolite mineral, analcime. Samples in the basin margin represent four rock types including 7 sandstone, 5 siltstone, 8 mudstone and 8 marlstone samples. Minerals which occur in abundance in the basin center include the common rock forming minerals quartz, albite and potassium feldspar, and iron-bearing dolomite; as well as the uncommon feldspar buddingtonite, and saline minerals nahcolite and dawsonite. In the basin center, four rock types are represented include 2 siltstone, 34 mudstone, 44 marlstone and 9 saline subaqueous evaporite samples (Supplemental File N).

4.1 Minerals Identified

A large set of over 35 minerals were identified in this study of the Green River Formation (GRF) in the Piceance Creek Basin (PCB). Fifteen of the 35 identified minerals are described as major phases, and the remaining twenty minerals are described as minor phases. Minerals are defined as a major or minor phase in this dataset by both occurrence and abundance according to a natural cut-off present in the dataset. Major phases are defined as being both present in over 10 samples of either basin location, and at over 5 wt% average abundance. Minor phases are accessory minerals that usually occur only in trace amounts, and are generally, but not necessarily less common. Minor phases are defined as minerals with abundances of less than 5 wt% average in both basin locations, even if they do occur in over 10 samples in either location. For example, pyrite is a minor phase because although it occurs in 80 out of 89 samples in the basin center, quantities are only 1.7 wt% average in the basin center, and 0.8 wt% average in the basin margin.
Major phases fall into four mineral categories: 1) framework silicates, 2) sheet silicates, 3) divalent Ca-Mg-Fe carbonates, and 4) saline minerals (sodium-bicarbonates, -carbonates and -chlorides). Minor phases fall into the same four mineral categories as major minerals, with the exception of framework silicates (all framework silicate minerals are abundant and common major phases), and additionally include sulfides, sulfates, phosphates, oxides, and hydroxides. Table 4.1 lists the major and minor minerals identified, listed by category, with chemical formulas.

**Table 4.1** List of minerals and chemical formulas identified in this study in the Green River Formation, Piceance Basin, divided into major and minor phases. Formulas for solid solution minerals are nominal compositions and do not reflect the exact composition of the phase identified. Mineral formulas from Deer et al. 1992.

<table>
<thead>
<tr>
<th>Major Phases</th>
<th>Minor Phases</th>
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<tbody>
<tr>
<td><strong>Major Framework Silicates</strong></td>
<td><strong>Minor Sheet Silicates</strong></td>
</tr>
<tr>
<td>Quartz</td>
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<tr>
<td>Potassium Feldspar</td>
<td>KAlSi₃O₈</td>
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<tr>
<td>Albite (Plagioclase)</td>
<td>NaAlSi₃O₈ - Ca(AlSi₃O₈)</td>
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<td>Buddingtonite</td>
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<tr>
<td>Analcime</td>
<td>NaAl₄Si₃O₁₀(6H₂O)•H₂O</td>
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<tr>
<td><strong>Major Divalent Carbonates (Ca, Mg, Fe)</strong></td>
<td><strong>Minor Divalent Carbonates (Ca, Mg, Fe, Mn)</strong></td>
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<tr>
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<td><strong>Minor Saline Minerals (Sodium Bicarbonates)</strong></td>
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</tr>
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</tr>
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</tr>
<tr>
<td><strong>Minor Divalent Carbonates (Ca, Mg, Fe)</strong></td>
<td><strong>Minor Oxides, Hydroxides and Other</strong></td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
</tr>
<tr>
<td>Ferroan Dolomite, Ankerite</td>
<td>Ca(Fe,Mg)(CO₃)₂</td>
</tr>
<tr>
<td><strong>Major Saline Minerals (Sodium Bicarbonates)</strong></td>
<td><strong>Minor Sulfides, Sulfates and Phosphates</strong></td>
</tr>
<tr>
<td>Dawsonite</td>
<td>NaAICO₃(OH)₂</td>
</tr>
<tr>
<td>Nahcolite</td>
<td>NaHCO₃</td>
</tr>
<tr>
<td>Halite**</td>
<td>NaCl</td>
</tr>
</tbody>
</table>

* Trioctahedral 2:1 Clays = biotite, phlogopite, biotite/vermiculite, or trioctahedral smectites

** Halite is a major phase, but intervals with high levels were not sampled for this study, therefore many calculations and figures include halite as minor/other

Mineral formulas from Deer Howie & Zussman, 1992
Framework silicates include quartz, potassium feldspar, plagioclase, buddingtonite (ammonium feldspar) and analcime (a zeolite), and are both the most common in occurrence, and the most abundant of all minerals identified. All five framework silicate minerals identified occur as major phases. At least 7 types of sheet silicates are identified. The major sheet silicates are the dioctahedral 2:1 clay minerals (illite, smectite, mixed layer illite/smectite, and mica). Trioctrahedral 2:1 clay minerals, chlorite and kaolinite comprise the minor clay phases, and are described as “other clays” in subsequent charts and tables.

The divalent carbonates are major phases in the GRF, referred to as Ca-Mg-Fe carbonates here, and include calcite and dolomite, with unusually high concentrations of iron-rich carbonate minerals. Eight separate calcium, magnesium, iron and manganese carbonate phases have been identified in total. The solid solution of dolomite, ferroan dolomite, and ankerite constitutes the major phase, which together with the minor phase kutnohorite, are collectively referred to as ferrodolomite for this study. Siderite, Mg siderite, Mg calcite, magnesite are the other minor iron-magnesium carbonate phases.

Saline minerals are an uncommon group of minerals that occur in high quantities in the GRF. The saline minerals include halite and sodium carbonate and bicarbonate minerals. The three major sodium salt phases identified are halite, nahcolite and dawsonite, and the two minor phases are northupite and natrite. Halite occurs as a major phase in the basin, but is classified as a minor phase in this dataset because no samples with high levels of halite were selected for this study.

Accessory mineral groups include sulfides, sulfates, phosphates, oxides, and hydroxides. These categories of minerals occur only in trace amounts and/or uncommonly and therefore are classified together in one group as “other” or “accessory minerals” for most purposes in this thesis, as the focus of this study is on major phases. Pyrite is the most common sulfide present, with marcasite being second in abundance. Gypsum, anhydrite, and barite are the three sulfates found, all in very small quantities. Phosphates include apatite and woodhouseite, (CaAl3(SO4)(PO4)(OH)6). Hydroxides and oxides include brucite, aluminum oxy-hydroxide, and anatase. For the purposes of a comprehensive interpretation of mineral relationships and distributions of mineral classifications, trace and uncommon minerals that belong to one of the four major categories (framework silicates, sheet silicates, Ca-Mg-Fe carbonates or saline minerals) are combined with quantities of the major phases from the same category for
calculations and charts. Examples include combining quantities of kutnorhorite with that of ferrodolomite, and including natrite and northupite concentrations with nahcolite.

Verification that mineral assemblages identified are complete is provided by comparison of ExxonMobil data from the Shell 23X-2 core, available from the USGS Core Research Center Database. Verification of the quality of mineral data is also achieved by comparison of the COSTAR John Savage 24-1, Shell 23X-2, and Douglas Pass sections to XRD relative peak height data from the CR-2 and CO-1 core sections by Dean et al. 1981; and Robb and Smith, 1974, respectively. The CR-2 and CO-1 datasets are semi-quantitative values, and are incomplete in that they include only 11 minerals in the CR-2 analysis, and 8 minerals in the CO-1 depth profiles. Both CR-2 and CO-1 lack buddingtonite, and the only clay mineral represented in CR-2 is illite. The CO-1 analysis includes no semi-quantitative values for clay minerals. The CO-1 core data also includes Fischer Assay and resistivity profiles (Dean et al. 1981; Robb and Smith, 1974).

4.2 Basin Distribution of Mineral Assemblages

Mineral assemblages of the GRF vary greatly by both location in the basin and stratigraphic interval. The basin center is richer in the number of distinct mineral phases present relative to the basin margin. Thirty-one different minerals have been identified from the basin center section. Twenty-four minerals were identified in the basin margin section samples. Mineral assemblages are illustrated in bar charts for the basin center in Figure 4.1 for 89 samples of the John Savage 24-1 and Shell 23X-2 sections, and for the basin margin in Figure 4.2 for 28 samples for the Douglas Pass section. Mineral phases are grouped by classification and normalized to 100% excluding organic matter. Halite is grouped into the category “other” along with accessory minerals, because although it is a major phase in the basin center, it does not occur in high quantities in samples included in this study. It is important to note while interpreting the basin center bar charts, that nahcolite and halite are soluble minerals. Nahcolite and halite are absent in these wells above a stratigraphically cross-cutting surface, from the lower part of Lean Zone L5, presumably due to post-depositional leaching by groundwater. Original deposition of saline minerals above this level is indicated by vugs and casts of nahcolite or halite nodules.
Quantitative results are summarized in Table 4.2 by location in the basin: basin center or basin margin. In the basin center, mineral assemblages are distinctive due to high proportions of the saline minerals nahcolite, halite, and dawsonite. Saline minerals occur only uncommonly and as minor phases in the basin margin. The basin center assemblage is also distinguished from the basin margin assemblage by the significant occurrence of buddingtonite throughout most of the section, in contrast to the margin, where buddingtonite is uncommon. In the basin margin, analcime is a common phase which occurs throughout the section, but is uncommon in the basin center. The remaining framework silicates (quartz, plagioclase and potassium feldspars) occur in roughly equal amounts in both the margin and basin center (Table 4.2). Sheet silicates occur in high quantities throughout the basin margin section, but clay minerals are only minor components in the majority of the basin center stratigraphic intervals, which is unusual for such a fine-grained formation (Boggs, 1992). Both the basin center and basin margin are rich in Ca-Mg-Fe carbonate minerals, but they occur in more consistent quantities throughout the basin center. The basin margin contains higher concentrations of calcite, whereas the basin center is dominated by iron-magnesium carbonate minerals. Trace and minor phases are more abundant in the basin center. The basin center is also much richer in organic matter than the basin margin section. In the basin margin, organic matter quantities are lower, and therefore more stable throughout the stratigraphic section, whereas in the basin center quantities demonstrate greater variability between intervals.

Mineral assemblages in the deeper stratigraphic section of Shell 23X-2 of the basin center (the “lower Shell” including stages S1 and lower S2 of the Shell 23X-2 core), share many similarities with assemblages in the basin margin (DP), as shown in Table 4.2. Most significantly, the lower basin center and the basin margin sections both have high clay mineral contents, and higher calcite:ferrodolomite ratios. Saline mineral quantities are also low to absent in both sections. Buddingtonite quantities are very low to absent in the basin margin, and it occurs in much lower relative quantities in the lower basin center than in the rest of the basin center sections (upper Shell and JS). Organic richness is also relatively lower in both the lower basin center and basin margin in contrast to much higher concentrations in the upper basin center sections. Concentrations of organic matter for the different basin locations are also illustrated in Figures 4.3 and 4.4, which were normalized to 100% to include organic matter, and break out clays into major and minor (other) phases. One major contrast between the mineral assemblages
Figure 4.1 Basin center bar chart of mineral assemblages of the John Savage 24-1 and Shell 23X-2 sections for 89 samples. Vertical axes are depth in feet, horizontal axes are normalized to 100% excluding organic matter. Units are in weight % on an inorganic mineral-only basis. Vertical labels are rich zones (in blue), lean zones (in pink), and lake stages (in green). Stages are S1, fresh or brackish lake, S2, transitional lake, S3, highly fluctuating lake, S4, rising lake, S5, high lake, and S6, closing lake. Upper and lower Shell divisions are defined by a major change in clay mineral content and roughly corresponds to the division between the Garden Gulch and Parachute Creek Members. Sections are hung at top of Stage S2. (Tänavsuu-Milkeviciene and Sarg, 2012)
Figure 4.2 Basin margin bar chart of quantitative mineralogy of the Douglas Pass section for 28 samples. Vertical axis is depth in feet, horizontal axis is normalized to 100%. Units are in weight % on an inorganic mineral basis. Vertical labels are rich zones (in blue) and lean zones (in pink), and lake stages (in green). Stages are S1, fresh or brackish lake, S2, transitional lake, S3, highly fluctuating lake, S4, rising lake, S5, high lake, and S6, closing lake (Tänavsuu-Milkeviciene and Sarg 2012).
Figure 4.3 Basin margin bar chart summary including organic matter, of the mineralogy of the Douglas Pass section. Clay mineral types are also broken out into two categories: dioctahedral 2:1 clay minerals (illite/smectite/mixed layer) and all other clay mineral types. Depth in feet on vertical axis. (28 samples, Chevron analyzed).

of the lower basin center Shell 23X-2 section and the basin margin Douglas Pass section is that the basin margin contains high amounts of analcime. Analcime is present only in trace quantities in the lower basin center Shell 23X-2 section, as well as in most of the stratigraphic section of the basin center.
Figure 4.4 Basin center bar chart summary including organic matter. Mineralogy of the John Savage 24-1 and Shell 23X-2 sections, with clay types detailed (54 samples, Chevron analyzed). Normalized to 100%.
Table 4.2 Quantitative results of major mineral phases by basin location, in weight % average. Basin center values are separated by core section and stratigraphic interval: John Savage 24-1 (JS) and Shell 23X-2 (Upper Shell and Lower Shell). The lower Shell 23X-2 interval is equivalent to the lower mineral unit, including lake stages S1 and lower S2. Divisions between the upper and lower Shell 23X-2 are to emphasize contrasts between the lower basin center (Lower Shell) and upper basin center (JS) assemblages, and similarities between the lower basin center and basin margin (DP) assemblages.

<table>
<thead>
<tr>
<th>Average wt%</th>
<th>Margin</th>
<th>Basin Center</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DP</td>
<td>Combined JS</td>
</tr>
<tr>
<td>Quartz</td>
<td>18.4</td>
<td>17.3</td>
</tr>
<tr>
<td>K Feldspar</td>
<td>14.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>8.1</td>
<td>7.8</td>
</tr>
<tr>
<td>Buddingtonite</td>
<td>0.2</td>
<td>8.5</td>
</tr>
<tr>
<td>Analcime</td>
<td>9.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Calcite</td>
<td>6.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Dolomite/Ankerite</td>
<td>11.5</td>
<td>21.8</td>
</tr>
<tr>
<td>Dawsonite</td>
<td>NA</td>
<td>7.6</td>
</tr>
<tr>
<td>Nahcolite</td>
<td>0.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Illite/Smectite</td>
<td>18.6</td>
<td>9.7</td>
</tr>
<tr>
<td>Other Clays</td>
<td>3.7</td>
<td>NA</td>
</tr>
<tr>
<td>Organic matter</td>
<td>7.1</td>
<td>12.4</td>
</tr>
</tbody>
</table>

4.3 Stratigraphic Distributions: Transition Zones, Mineral Units

Two significant stratigraphic changes in mineral proportions are recognizable in the basin center cores of the GRF of the Piceance Basin, and will be referred to as the upper and lower transition zones. The upper and lower transition zones are defined by a simultaneous and significant shift in the proportions of quartz, clay minerals, and feldspars. An appearance or disappearance of both dawsonite and buddingtonite is also associated with the lower and upper transition zones, respectively. Change in the proportions of ferrodolomite, siderite and pyrite are also evident. The locations and character of the upper and lower transition zones are especially evident in the depth plots of the CR-2 and CO-1 sections, which with 782 and 1072 samples respectively, provide very high resolutions (Figures 4.5 and 4.6). Basin center depth profile results for the John Savage 24-1 and Shell 23X-2 sections exhibit similar mineral transition zones, with approximately the same stratigraphic location as recognized in the CR-2 and CO-1
datasets (Figures 4.7 and 4.8). Transitions are less recognizable in the basin margin section, and stratigraphic changes in mineralogy that do exist are of a different character, so the discussion of the two major transition zones will focus on the basin center sections. Figure 4.9 shows depth plots for the basin margin at the Douglas Pass, including stratigraphic column and gamma ray profile.

Three mineral units (MU) are defined by the division of the stratigraphic column into intervals above, between and below the upper and lower transition zones. The lower MU extends from the base of the GRF up to the lower transition zone; the middle MU is between the lower and upper mineral transition zones, and the upper MU extends from the upper mineral transition zone through the top of the GRF. The upper transition zone generally occurs near the top of rich zone R5, corresponding to the upper part of Stage S3, the rapidly fluctuating lake stage. The lower transition zone occurs around the middle of rich zone R2, corresponding to the lower part of Stage S2, the transition from the freshwater stage to more saline conditions, and near to the division between the Garden Gulch and Parachute Creek members (Dean et al., 1981; Robb and Smith, 1974). The two transition zones are not chronostratigraphic horizons, but rather zones that cover an interval of variable thickness in each core. In some sections, the transition zones correspond with shifts in the Gamma Ray profiles. Gamma Ray profiles are included in the depth plots of Shell 23X-2 and the Douglas Pass.

The lower MU in the basin center is characterized by being relatively rich in quartz, calcite, and clay minerals. The middle MU in the basin center is reduced in quartz by 34%, and clay minerals by 94%, whereas potassium feldspar increases by four times and buddingtonite increases by over two times. The saline minerals dawsonite and nahcolite become major components of the assemblage, and quantities of organic matter increase. The upper MU in the basin center is richest in feldspars and ferrodolomite, and poorest in quantities of quartz. The saline minerals dawsonite and nahcolite, and quantities of buddingtonite are again greatly reduced. Clay minerals and calcite are relatively richer in the upper MU of the basin center. Average weight percent of all major phases are shown for each mineral unit by basin location in Table 4.3. Tables of quantitative mineral results by lake stage are available in Supplemental File P.

Results of this thesis are shown juxtaposed with the stratigraphic columns from core and outcrop descriptions, showing grain size, facies associations, and Fischer Assay profiles.
Table 4.3 Three mineral units (MU) defined as the intervals between transition zones and the weight per cent average of major mineral phases for the two basin locations. Lake stages and rich and lean zones represented by the minerals units are indicated. Values are conditionally formatted to reflect average concentrations over 10 weight % as pink cells. Basin margin includes the Douglas Pass outcrops. Basin Center includes the John Savage 24-1 and Shell 23X-2 sections. Tables of quantitative mineral results by lake stage are available in Supplemental File P.

<table>
<thead>
<tr>
<th>Weight % Average</th>
<th>Basin Margin</th>
<th>Basin Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Unit</td>
<td>Lower</td>
<td>Middle</td>
</tr>
<tr>
<td>Stages</td>
<td>S1-S2</td>
<td>S2-S3</td>
</tr>
<tr>
<td>Rich/Lean Zone</td>
<td>R0-R2</td>
<td>R2-R5</td>
</tr>
<tr>
<td>Quartz</td>
<td>22.6</td>
<td>20.8</td>
</tr>
<tr>
<td>K Feldspar</td>
<td>7.2</td>
<td>18.9</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>6.0</td>
<td>10.2</td>
</tr>
<tr>
<td>Buddingtonite</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Analcime</td>
<td>12.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Calcite</td>
<td>4.6</td>
<td>6.2</td>
</tr>
<tr>
<td>Ferrodolomite</td>
<td>7.0</td>
<td>9.1</td>
</tr>
<tr>
<td>Dawsonite</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Nahcolite</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Illite/Smectite</td>
<td>23.9</td>
<td>19.1</td>
</tr>
<tr>
<td>All Other Clays</td>
<td>4.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Organic matter</td>
<td>6.8</td>
<td>7.8</td>
</tr>
<tr>
<td>Accessory Minerals</td>
<td>2.8</td>
<td>0.3</td>
</tr>
</tbody>
</table>

modified from Tänavsuu-Milkeviciene and Sarg, (2012). The Shell 23X-2 figure also includes a gamma ray profile. Legends for the facies associations illustrated in the stratigraphic columns are shown for the basin center and margin sections. Results are presented in Figures 4.7, 4.8 and 4.9 with the same set of 11 minerals as given in the CR-2 depth plot, and the addition of buddingtonite, to make 12 in total. Minerals are in the same order from left to right: 1) quartz, 2) illite-smectite (illite in CR-2), 3) analcime, 4) plagioclase (albite in CR-2, Na-feldspar in CO-1), 5) potassium feldspar, 6) buddingtonite, 7) dawsonite, 8) nahcolite, 9) calcite, 10) ferrodolomite (dolomite in CR-2 and CO-1), 11) siderite (Mg-siderite in CR-2), and 12) pyrite. The Douglas Pass margin mineral set also includes 3) other clay minerals and 11) organic matter, and is missing 7) dawsonite (not present) for a total of 13 minerals.
Figure 4.5 CO-1 core basin center depth plots for 8 minerals, from semi-quantitative relative peak height measurements. Clay minerals and buddingtonite are not included in this dataset. Depth in feet, Fischer Assay oil yield in gallons per ton, and resistivity profiles provided on the left axis. Stratigraphic units on the left vertical axis, lake stages and rich zones marked on the right side. Rich zones are shaded gray, lean zones are white. Upper and lower transitions marked with blue lines. Modified from Robb and Smith, 1974. An enlarged version of this figure is given in Supplemental File R.
CR-2 Depth Plots (Semi-quantitative)
Relative Amounts of Major Minerals by XRD Peak Height

<table>
<thead>
<tr>
<th>Quartz</th>
<th>Illite</th>
<th>Analcime</th>
<th>Albite</th>
<th>K-feldspar</th>
<th>Dawsonite</th>
<th>Na hornite</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Mg-Silicate</th>
<th>Pyrite</th>
</tr>
</thead>
</table>

Modified from Dean, Pitman, and Harrach, 1981

**Figure 4.6** CR-2 core basin center plots of depth vs. semi-quantitative relative peak height measurements by XRD for 11 minerals. Buddingtonite is not included and illite is the only clay mineral in this dataset. Depth is in feet on the vertical axis, and lake stages and rich and lean zones are marked on the right side. Rich zones are shaded gray, lean zones are white. Upper and lower transitions are marked with a blue line. Modified from Dean et al, 1981. An enlarged version of this figure is given in Supplemental File S.
In the basin center, the highest concentrations of quartz are observed below the lower transition zone (24 wt% ave), in the lower MU. Abundance then decreases sharply to 16 wt% ave. in the middle MU (Table 4.3; Figure 4.8). Quantities of quartz then decrease again at the upper transition zone to less than 10 wt% ave. in the upper MU (Figure 4.7). A similar pattern is observed in the basin margin, where quartz also generally decreases upsection (Figure 4.9). Feldspar quantities increase greatly at the lower transition zone of the basin center, with K-feldspar quadrupling from 2.6 to 10.6 wt% ave. in the middle MU. A simultaneous decrease in the abundance of clay minerals also occurs at the lower transition zone in the basin center (Figure 4.6). Total clay minerals are the dominant component in the lower MU, with an average of 32 wt%, and as high as 51% maximum. Above the lower transition zone, the middle MU is relatively devoid of all clay minerals in the saline zone, with an average of less than 2 wt% (Figure 4.8). In the upper MU, clay minerals return, but remain at moderately low concentrations of 7 wt% ave. In the basin margin, the highest total clay mineral abundances also occur in the stratigraphic equivalent of the lower MU of the basin margin (Figure 4.9).

Minor clay minerals show an uneven stratigraphic distribution in the basin margin, as illustrated in the barchart of clay mineral types in Figure 4.10. Kaolinite and chlorite are most abundant throughout the equivalent lower and middle MU. Trioctahedral 2:1 clay minerals do not appear until near the equivalent middle MU, and are most common in lake stages S3 and S4. In the basin margin equivalent of the upper MU, minor clay minerals are nearly absent.

Analcime is distributed throughout the basin margin section, but is found in the highest amounts in samples from the stratigraphic equivalent of the lower and upper MUs at 12.5 and 12.1 wt% ave. (Table 4.3; Figure 4.9). The lowest amounts of analcime in the basin margin are found in the equivalent of the middle MU. In the basin center, analcime is completely absent in the saline zone of the middle MU, and occurs in the upper MU at only 1.4 wt% ave., and only in one sample in the lower MU (Table 4.3; Figures 4.7 and 4.8). Dawsonite is first detected in the basin center at the lower transition zone and then decreases to nearly trace quantities again at the upper transition zone and, therefore, dawsonite deposition is one factor used to define the position of the transition zones (Figures 4.5, 4.6, 4.7 and 4.8).
Figure 4.7 Basin Center John Savage 24-1 depth plots (ft) of quantitative XRD values of 12 minerals from the upper basin center section. Blue line marks upper transition zone. Lake stages, rich zones shaded gray, lean zones in white, Fischer Assay in gal/ton and stratigraphic column on the left vertical axis. Legend gives facies associations for basin center John Savage 24-1 and Shell 23X-2 cores, modified from Tänavsuu-Milkeviciene and Sarg, (2012). An enlarged version of this figure is given in Supplemental File T.
Figure 4.8 Basin Center Shell 23X-2 depth plots with quantitative XRD values for 12 minerals from the lower stratigraphic section. The lower transition zone is marked as a blue line. Stratigraphic members, lake stages, rich zones shaded gray, and lean zones in white are marked on left vertical axis. Depth in feet. Gamma ray profile, Fischer Assay, and Stratigraphic column, modified from Tänavsuu-Milkeviciene and Sarg, (2012). Legend of facies associations for stratigraphic column of basin center in Fig. 4.7. Modified from Tänavsuu-Milkeviciene and Sarg (2012). An enlarged version of this figure is given in Supplemental File U.
Figure 4.9 Basin Margin Douglas Pass outcrop depth plots with quantitative values for 13 mineral phases. The vertical axis is depths in meters, and stratigraphic members, lake stages, and rich and lean zones are marked on the left side. Rich zones are shaded gray, lean zones are white. Stratigraphic column and gamma ray profile are on the vertical axis to the left. Legend identifies facies associations of the basin margin illustrated in the stratigraphic column. Upper and lower transitions are not marked because their presence is not obvious in the margin. Depth in feet on vertical axis. Modified from Tänavsuu-Milkevičiene and Sarg, (2012). An enlarged version of this figure is given in Supplemental File V.
Figure 4.10 Clay mineral types in the basin margin, are shown for 28 samples from the Douglas Pass section, by weight %, relative to lake stages and rich and lean zones. Illite/smectite is the only clay mineral type present throughout the entire section. Kaolinite occurs only in stages S1 through the base of S3, chlorite occurs only in upper stage S1 through S3, and trioctahedral 2:1 clays occur only in stages S2 through S4. Height in section in feet on vertical axis.
Buddingtonite is first found in significant amounts at the lower transition zone and is greatly reduced at the upper transition zone. Buddingtonite averages 10.9 wt%, and dawsonite 11.1 wt% ave in the middle MU (Table 4.3). Although buddingtonite and dawsonite have parallel stratigraphic occurrences, and both are most abundant in the middle MU, surprisingly, no quantitative relationship could be found between the two minerals. The first deposition of nahcolite occurs above the lower transition zone in a later part of the middle MU in the basin center, at 14.5 wt % ave. XRD detection of nahcolite ceases near the upper transition zone, although nodules continued crystallizing in the leached zone extending into the upper MU (Figures 4.5, 4.7 and 4.8).

Calcite occurs throughout the stratigraphic section in the basin margin, but is highest in abundance in the equivalent upper MU at 9.1 wt% ave. (Table 4.3; Figure 4.9). In the basin center, calcite is only detected above trace quantities in the lower and upper MU in the same intervals that clay minerals are most abundant (Figures 4.7, 4.8). Calcite is nearly completely absent in the saline zone of the middle MU. This distribution of calcium carbonate minerals is also reflected by the elemental calcium concentrations in the upper and lower MUs of the basin center, relative to the sum of elemental calcium, magnesium and iron (Figure 4.11). Siderite is most abundant in the basin center lower and middle MU (Figures 4.7 and 4.8). Ferrodolomite is present in large quantities throughout the basin center section, but is most abundant in the middle and upper MUs, at 22.6 and 25.4 wt % ave., respectively. In the basin margin, ferrodolomite is the predominant Ca-Mg-Fe carbonate species in the equivalent upper MU, at 18.7 wt% ave. Ferrodolomite quantities are more variable in the basin margin, and the lowest concentrations occur in the stratigraphic equivalent lower MU at 7.0 wt % ave..

The highest quantities of organic matter are found in the basin center; at 9.3 wt%, 13.2 wt%, and 11.7 wt% ave. in the lower, middle, and upper MUs, respectively (Table 4.3). In the basin margin, the occurrence of organic matter is less variable and present in roughly half to two-thirds the quantities of the basin center according to XRD methods (Supplemental File L). Organic matter is present at an average of 6.6 wt%, 7.8 wt%, and 6.8 wt% ave. respectively, in the lower, middle, and upper MU stratigraphic equivalents of the basin margin. The highest concentrations of pyrite occur in the lower MU of the basin center, with an average of 2.4 wt% in the Shell 23X-2 section.
**Figure 4.11** Depth Plot of Calcium as a proportion of the sum of elemental calcium, magnesium and iron in the basin center, as a proxy for the ratio of calcite to all other Ca-Mg-Fe carbonates. Higher calcium abundance occurs in the lower stratigraphic intervals in stage S1 and lower S2, and in the upper intervals of stages S4, S5 and S6. Depth in feet on vertical axis.
4.4 Authigenic Mineral Phases

Minerals of the GRF have many origins, and in many cases, one mineral phase may have multiple origins. These origins include detrital (allogenic) deposition, chemical precipitation from the water column, authigenic formation in pore waters at or below the sediment-water interface, and diagenetic formation during early burial. Characteristics which identify secondary minerals as being authigenic in origin may include purity of composition, fine grain size, recrystallized and replacement textures, and euhedral or angular delicate crystal faces indicative of in-situ growth and lack of transport. By contrast, signs of transport in a detrital grain include anhedral grain boundaries, microfractures, rounding, and alignment with bedding (Boggs, 1992; Deer et al. 1992).

Optical petrography and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) were employed to assist in identification and recognition of evidence of authigenic origins. Most of the thin section samples were too fine-grained for optical petrography to be effective, and the majority of the authigenic minerals have nearly identical optical properties, making them difficult to distinguish. The four thin sections that were analyzed by SEM-EDS are mudstone and saline subaqueous evaporite rock types from the basin center John Savage 24-1 section (Figure 3.1).

The four thin section samples were chosen based on prior optical petrographic screening for authigenic textures, and XRD results indicating high quantities of the rare minerals buddingtonite, dawsonite, and nahcolite were present. Low energy photons for low atomic number elements are strongly absorbed in the sample, and therefore show significantly reduced count rates. Carbon, nitrogen and oxygen signals are unrecognizable above background, causing saline and other carbonate-bearing minerals, and nitrogen-bearing buddingtonite to be especially difficult to identify (Krohn et al. 1993; Ramseyer, 1993, Skok, personal communication; 2013). EDS spectral patterns for sodium also show low peak heights in sodium-bearing minerals, including albite and dawsonite for the same reason (Figure 4.12). (Ramseyer, 1993; Skok, personal communication, 2013).

Buddingtonite could not be identified by either optical petrography or by SEM-EDS. Pure buddingtonite \((\text{NH}_4\text{AlSi}_3\text{O}_8\cdot0.5\text{H}_2\text{O})\) would give an EDS spectrum solely consisting of Si and Al peaks in an approximate 3:1 ratio, because nitrogen is undetectable, but this pattern was not identified. Pure buddingtonite may not be present if it is in continuous solid solution with
Figure 4.12 Representative EDS spectral pattern for pure end-member albite, indicative of an authigenic origin for feldspar in the basin center. The Na peak is attenuated due to its low atomic number. John Savage 24-1 sample JS-45, from 2355 ft depth, at the base of rich zone R5 in Stage S3. Thin sections were coated in gold, accounting for the Au peak.

Other feldspars, produced by possible substitution of NH<sub>4</sub> for K, and therefore only EDS spectra containing K, Si, and Al would exist (Barker, 1964; Loughnan 1983). Buddingtonite may also occur as a mixture of microcrystals with other minerals, in fine matrices in association with illitic precursors, or as thin overgrowths on existing feldspar grains and other minerals (Krohn et al. 1993; Oh et al., 1993; Ramseyer, 1993). It is also possible that buddingtonite did not occur in the few thin sections chosen for SEM analysis (although XRD results of the larger sample show significant quantities). Most feldspar grains identified by SEM-EDS in the basin center samples were pure end-member albite or K-Feldspar (Figures 4.12 and 4.13). Only a small portion of the grains tested showed any calcium peaks in conjunction with the set of elements Si, Al, or Na in the four basin center samples tested. A small Ca peak did occur with a few K-Feldspar patterns, which may be due to proximity to calcite cement.

The four samples analyzed by SEM-EDS contained both halite and nahcolite according to XRD analysis, but neither were detectable under the EDS beam. Nahcolite was recognized with diverse morphologies by optical petrography and in backscatter SEM imaging, from massive
Figure 4.13 EDS spectral pattern showing pure end member composition for potassium feldspar with appropriate peak proportions for the mineral formula of 1:1:3 of Al:K:Si. Basin center John Savage 24-1, sample JS-45. Thin sections were coated in gold, accounting for the Au peak.

Figure 4.14 Authigenic textures of analcime (left) and nahcolite (right). Characteristic fine-grained "soccer balls" of analcime (left), in the margin Douglas Pass section. Plane polarized light, 4x magnification. Nahcolite as a fracture filling cement (right) in the margin Douglas Pass. Cross polarized light, 10x magnification.

laminations in the basin center, to pore and fracture-filling phases in the margin, but identification could not be confirmed (Figures 4.14, and 4.16).
Analcime and dawsonite were identified as fine, euhedral grains with optical microscopy. Round ("soccer ball") crystals from the basin margin Douglas Pass section are typical of analcime. Dawsonite occurs in two distinctive crystal forms as observed in thin section, acicular, and equant grains, both displaying prominent cleavage (Figures 4.15, 4.16, 4.17). Delicate acicular crystals of dawsonite are intact and randomly oriented, indicating a lack of transport. Acicular grains are relatively large and visible with a light microscope at only 4x magnification. The equant form of dawsonite grains are finer than the acicular forms, and are only recognizable under an SEM at over 500x magnification, commonly with a hexagonal cross-section. Corresponding EDS spectral patterns showed a small Si peak, in addition to Al and Na, in around two-thirds of points sampled within equant dawsonite grains (Figure 4.18).

Evidence found of the authigenic origins of feldspars in the GRF include very fine grain sizes, euhedral crystal forms, and SEM-EDS spectral patterns showing high purity end member compositions (Figure 4.16) (Boggs, 1992; Deer et al. 1992). In the GRF, most detrital members of the framework silicates identified in this study also commonly occur as authigenic phases.

Figure 4.15 Two distinct crystal forms of dawsonite. Left, equant dawsonite grain with prominent cleavage of about 25 microns diameter (0.025mm), backscatter SEM image at 1600x magnification. Basin center, John Savage 24-1, sample JS-71. Right, delicate acicular dawsonite about 100 microns in length (0.1mm) from the basin center John Savage 24-1 section, illustrating an authigenic texture. Sample JS-35, plane polarized light, 25 x magnification.
Figure 4.16 SEM images of authigenic minerals in the basin center, John Savage section. A) massive nahcolite, euhedral feldspar grains, primary feldspar which appears altered, equant grain of dawsonite. 1000x, backscatter. B) Euhedral lath of sodium feldspar, surrounded by groundmass of other euhedral tabular feldspars grains. Most fine, rounded and anhedral grains are ferrodolomite and quartz. Large equant grain on the upper right is dawsonite. 1300x SE. C) Euhedral, tabular crystal of albite, smaller euhedral grain of potassium feldspar, in a groundmass containing anhedral and euhedral grains of feldspars, quartz and ferrodolomite. 850x, backscatter. D) Large lath of dawsonite in a groundmass containing anhedral quartz, equant dawsonite, and anhedral and euhedral feldspars, and muscovite. 1200x, SE.
Figure 4.17 SEM images of Ca-Mg-Fe carbonate grains in basin center, Stage S3, samples JS-35 (left) and JS-71 (right). Two relatively coarse ferrodolomite grains, one rimmed by pyrite, surrounded by a groundmass containing finer grains of potassium feldspar and quartz (left). Coarser grain to the left is anhedral, equant dawsonite, SE image. Relatively large anhedral ferrodolomite grain (right), adjacent to pure end member common feldspar grains. Matrix is composed of Ca, S, Al, Si, K and Cl, 800 x SE image.

Figure 4.18 SEM-EDS spectra identifying dawsonite, without a peak for Si, distinguishing it from the EDS signature used to identify albite or analcime (since carbon cannot be detected), and from lone peaks of Al and Si expected for buddingtonite. Thin sections were coated in gold, accounting for the Au peak.
4.5 Mineral Quantification and Occurrences

The following is a summary describing the significant characteristics of each major and minor phase, in terms of abundances and frequency of occurrences, for each major mineral class. Solid solutions, individual species of larger mineral classes, detection challenges and anomalies are addressed.

4.5.1 Framework Silicates: Quartz, Feldspars, Analcime

The framework silicates are the dominant and most ubiquitous mineral class in the GRF. Quartz and Ca-Na-K feldspars, are found in every sample in both the basin margin and basin center. The unusual framework silicates, buddingtonite and analcime, have more localized occurrences, where analcime is common and abundant only in the basin margin, and buddingtonite is a major phase only in the basin center. This group of minerals has the lowest error associated with quantification because they are well-crystallized, abundant, and produce sharp XRD peaks. The feldspar minerals occur in unusually high proportions in the GRF compared to most sedimentary rock (Boggs, 1992), of up to 44 wt% potassium feldspar, up to 38 wt% plagioclase, and up to 43 wt% buddingtonite. A majority of rock types are therefore arkosic.

Quartz is usually the most abundant framework silicate mineral in sedimentary rock, due to its resistance to weathering and alteration. This is not necessarily true in the GRF, where quartz is a dominant phase only in the lower MU of both basin locations. Values in the GRF for quartz are all low relative to the 30% average shale content reported in Boggs (1992). Overall, quartz quantities are nearly equivalent between the basin locations. The margin has an average of 18 wt%, compared to 17 wt% in the basin center (Table 4.2). The maximum quantity of quartz in any sample in this study is 49 wt%, which occurs in a sandstone of the basin margin that also contains 31% feldspar.

Feldspars include sodic and calcic plagioclase, potassium feldspar, and buddingtonite. Potassium feldspar is the dominant species of feldspar in samples of both basin locations in the GRF. This study is focused on quantifying major mineral phases, so no attempt was made to quantify the specific members of the common feldspar solid solutions present. While choosing minerals present in each sample during manual XRD pattern interpretation, many specific
feldspar members were selected to match peaks present, but this was not recorded for each sample or quantified individually. Quantitative results were lumped by the XRD software into the two general categories of plagioclase and potassium feldspar when calculating quantities. Individual feldspar members were identified and quantified using JADE software for the five John Savage 24-1 samples which were reanalyzed, and include bytownite, microcline, orthoclase, sanidine, albite and labradorite, shown in Supplemental File F. In the basin center CO-1 section, Robb and Smith (1972) stated that feldspars tentatively identified included low-temperature albite, sanidine, microcline, orthoclase, and adularia (Robb and Smith, 1974). Other evidence of more specific feldspar member identification is from the limited thin section SEM-EDS analysis performed on four basin center samples. Most feldspar grains identified by SEM-EDS in the basin center were pure end-member albite or K-Feldspar (Figures 4.12 and 4.13). Only a small portion of the grains tested showed any calcium peaks in conjunction with the set of elements Si, Al, or Na in the four basin center samples tested. A small Ca peak did occur with a few K-Feldspar patterns, which may be due to proximity to calcite cement.

Buddingtonite is a rare hydrated ammonium feldspar which occurs both commonly and abundantly in the basin center of the GRF. In the basin margin, buddingtonite is only a minor phase with a maximum occurrence of 3 wt%, and was detected in only two samples in this study. In the basin center, it was found in 85 of the 89 samples, with an average concentration of 8.5 wt%. It is most abundant in the middle MU of the basin center John Savage 24-1 section, at up to 43 wt%.

Analcime, NaAlSi$_2$O$_6$ · H$_2$O, is a low-silicon, hydrated framework silicate, and the only zeolite identified in this study of the Piceance Basin. No other zeolite was detected, even at trace levels. Analcime is much more abundant in the margin, where it is found in 26 of 28 samples, than in the basin center, where it is found in only 8 of 89 samples. Analcime occurs in high concentrations in the basin margin, at up to 37 wt%, but in only trace amounts in the basin center, with only 4 wt% at most. Overall, analcime occurs in the basin margin samples at 9 wt% average, and in the basin center at 0.3 wt% ave. Analcime was not identified in any of the 35 Shell 23X-2 samples analyzed by ExxonMobil, but it was found in one of the 15 Shell 23X-2 samples analyzed by Chevron.
4.5.2 Sheet Silicates: Clay Minerals

The major sheet silicates in the GRF are smectite, illite, mixed layer illite/smectite (I/S), and muscovite. Chevron’s bulk XRD analysis software classifies these phases as one solid solution group under the heading “dioctahedral 2:1 clays.” Minor sheet silicates include kaolinite, chlorite and “trioctahedral 2:1 clays.” Trioctahedral clay minerals may include biotite, phlogopite, biotite/vermiculite, or trioctahedral smectites, but the actual components were not specified in the report. Sheet silicates were determined by bulk XRD analysis, and were not isolated from other minerals for a separate clay-specific XRD scan. Sheet silicates have the largest error associated with quantification because peaks are broad for sheet silicates. In addition, primary peaks for clay minerals occur in the 2-theta range below 19 in the XRD spectra, where there is interference from background. Total clay mineral contents are greatest in the basin margin section, with an average of 22 wt%. Total clay mineral abundances are much lower in the basin center at only 10 wt% average. The fact that clay minerals are not a dominant phase in the fine-grained sediments of the upper basin center (middle and upper MUs) is a distinctive characteristic of the GRF. Much of the finest-grained material in the basin center is composed of feldspars, quartz, Ca-Mg-Fe carbonate minerals and saline minerals.

Dioctahedral 2:1 sheet silicates are the dominant clay mineral types in both basin locations and all stratigraphic intervals. In the basin margin, dioctahedral 2:1 clay minerals compose almost 19 wt% ave. of all samples, and total clay minerals are 22 wt% ave. Muscovite is not reported separately, but is included in dioctahedral 2:1 clay minerals by Chevron’s software, assuming equivalence to end-member mature illite (Deer et al. 1992). Muscovite/sericite was quantified in five John Savage 24-1 samples that were analyzed with JADE software, and identified in two of the samples. One sample in stage S3 contains 23 wt% muscovite and no illite or any other clay minerals.

Minor clay minerals concentrate in the margin, including kaolinite, chlorite, and trioctahedral 2:1 clay minerals. Minor sheet silicates in the margin are both more abundant and diverse than in the basin center samples. The basin center is nearly devoid of any minor clay mineral types. Minor clay minerals occur collectively at 3.6 wt% ave. in the margin, and as high as 19 wt%. Kaolinite occurs in the margin at 14 wt% maximum, chlorite as high as 4 wt%, and trioctahedral 2:1 clay minerals at a maximum of 9 wt%. Kaolinite is the only minor sheet silicate
that occurs in the basin center, at less than 1 wt% in all samples. There are no trioctahedral 2:1 clay minerals, or chlorite present in the basin center samples. Kaolinite was not identified in the set of basin center samples analyzed at Chevron, but the Shell 23X-2 data analyzed by ExxonMobil shows that it is present. Comparing the two datasets for Shell 23X-2 serves as verification of the quality of the bulk XRD clay mineral results. Neither of the two methods detected any other clay mineral types in the basin center other than kaolinite or dioctahedral 2:1 clay minerals. Minor clay minerals are also referred to as “other” clays in this study, relative to illite/smectite which is much more abundant and common. Minor clay minerals are illustrated as “other clays” versus major clay mineral as a proportion of total minerals in figures 4.3 and 4.4.

XRD clay mineral separates were not performed for this study. Therefore, in clay mineral–rich samples, dioctahedral 2:1 layer clays were refined using cation exchange capacity (CEC) to distinguish between illitic, mixed-layer illite-smectite, or smectitic samples. Any muscovite present is considered illitic, as it exhibits similar cation exchange properties (Bardon et al. 1993). Results of CEC analysis show that dioctahedral 2:1 clay minerals in the Douglas Pass margin sections are more smectitic than in the basin center sections. The majority of basin margin samples are smectitic and mixed I/S of intermediate smectite content. Only two basin margin samples are illitic (Figure 4.19).

Basin center samples are mainly illitic (or muscovitic) and mixed illite/smectite. In the basin center, Shell 23X-2 samples are dominated by illitic clay minerals in the lower MU, but John Savage 24-1 samples are primarily mixed I/S in the middle and upper MU (Figure 4.19). Only three samples in the basin center are smectitic. The two John Savage 24-1 samples that are smectitic have only 5 wt% total clay minerals, and are both in the middle MU. The one Shell 23X-2 sample that is smectitic has a very low total clay mineral content at the lower transition zone. Total clay mineral contents are lower in samples from the upper MU of the basin center John Savage 24-1 section, resulting in higher uncertainty. A complete table of the results of cation exchange capacity for clay mineral-rich samples analyzed are given in Supplemental File K Clay Mineral Data C.E.C.
Figure 4.19 Cation Exchange Capacity results for dioctahedral 2:1 clays, in milliequivalents per 100 grams, for 48 CEC samples from John Savage 24-1 (JS), Shell 23X-2 and Douglas Pass (DP) sections, by depth. Cut-off values defining illitic and smectitic compositions are shown as red and green vertical lines. Samples with values between 20 and 55 meq/100g, are defined as having intermediate smectite layer content, which may be mixed-layer or just a physical mix of illite and smectite (Bardon et al. 1993).

4.5.3 Ca-Mg-Fe Carbonate Minerals

Ca-Mg-Fe carbonate minerals are the most abundant mineral constituents in the basin center. In the basin margin, Ca-Mg-Fe carbonate minerals are one of the three most abundant mineral groups, with roughly equal proportions with quartz and clay minerals (Table 4.2). Major common Ca-Mg-Fe carbonate minerals identified in the GRF include calcite; and dolomite, ferroan dolomite, and ankerite (Ca(Fe,Mg,Mn)(CO₃)₂). The solid solution dolomite-ankerite is termed ferrodolomite for this thesis. Minor common Ca-Mg-Fe carbonate minerals identified in
this study are aragonite, Mg-calcite ((Ca,Mg)CO$_3$), siderite (FeCO$_3$), Mg siderite ((Fe,Mg)CO$_3$), magnesite (MgCO$_3$), and kutnohorite (CaMn(CO$_3$)$_2$).

Basin margin samples have an average of 18.1 wt% total Ca-Mg-Fe carbonate minerals, and basin center samples have an average of 26.2 wt% total Ca-Mg-Fe carbonate minerals. Ferro-magnesian types predominate over calcium carbonate minerals in most basin locations and stratigraphic intervals of the GRF (Figures 4.1, 4.2). Ferrodolomite is most common in the basin center, occurring in 100% of the 89 samples, whereas calcite occurs in just 60% of the samples (Figure 4.1). Calcite is more common and abundant in the basin margin samples, where it present in 82% of the 28 samples, and ferrodolomite occurs in 85% of the samples (Figure 4.2). In the margin, ferrodolomite quantities range from 0 to 60 wt%, and calcite from 0 to 46 wt%. Ferrodolomite has a smaller range of values from 1 to 46 wt% in the basin center sample set, and calcite a wider range from 0 to 61 wt%.

Ferroan dolomite is the member of intermediate composition in the solid solution dolomite - ankerite, defined by Deer et al. (1992) as having up to 20 molar % Fe substitution of Mg in Ca(Fe,Mg)(CO$_3$)$_2$. Magnesium-free ankerite (CaFe(CO$_3$)$_2$) does not exist in nature, but has been reported with up to 70% substitution of Mg by Fe (Deer et al., 1992). The basin center samples are about twice as rich in ferrodolomite as the basin margin. Ferrodolomite occurs at an average of 11.5 wt% in the margin, and 22 wt% ave. in the basin center (Figures 4.7, 4.8, and 4.9). Most XRD patterns in this study exhibited relatively broad peaks in the dolomite range, suggesting a wide range of substitution by iron. GRF sediments likely contain the entire range of naturally occurring ferrodolomite compositions, from pure calcium-magnesium dolomite to high iron-content ankerite. Evidence that dolomite is ferroan and that ankeritic values (>20% substitution of Mg by Fe) exist in the GRF of the PCB also includes SEM-EDS analysis, and inorganic chemistry, as well as XRD results by JADE (Supplemental File F). Relatively high iron contents in Ca-Mg-Fe carbonate minerals are indicated by SEM-EDS patterns in the basin center with Fe associated with Mg and Ca peaks (Figure 4.20), and by results of chemical analysis for elemental iron concentrations, relative to elemental calcium and magnesium. Fe content of dolomite-ankerite is variable, and potentially high enough in some samples to call the mineral ankerite after the definition by Deer et al. (1992). Pyrite is also a source of high elemental iron in many samples. Clay minerals also contribute both Mg and Fe, which are not
abundant in the middle and upper MUs of the basin center section, where ferrodolomite is the most abundant.

Aragonite is an uncommon calcium carbonate phase in the sample set of this study. Aragonite occurs in only 7 samples out of all 117 in the study, and 6 of those samples are in the basin center. In most samples, aragonite occurs in only trace amounts. Five of the six samples in the basin center are in the upper MU and have average concentrations of only 1.3 wt%.

Aragonite occurs at 26 wt% in a single sample in stage S5 of the upper MU in the basin center. The minor Ca, Mg, Fe and Mn carbonate minerals are rarely volumetrically significant in sedimentary rocks (Boggs, 1992). In this study, the minor Ca-Mg-Fe carbonate minerals include Mg-calcite ((Ca,Mg)CO₃), siderite (FeCO₃), Mg-siderite ((Fe,Mg)CO₃), magnesite (MgCO₃), and kutnohorite (CaMn(CO₃)₂). Mg-calcite was identified in this study as a trace phase in five samples in the basin margin, and in two samples in the basin center sample sets. It is found in the basin margin at up to 3.0 wt%, and in the basin center samples at a maximum of 1.2 wt%.

Magnesium calcite is a low temperature mineral and common component of many organisms such as calcareous algae (Deer et al., 1992). Organisms create their shells from aragonite just as commonly as from calcite, and therefore, where calcite occurs, aragonite is usually also present or had been present prior to diagenetic alteration (Deer et al. 1992). Therefore, it is very likely that many of these minerals were present at much higher concentrations prior to dolomitization (Boggs, 1992).

Siderite is generally a rare mineral in sedimentary rocks, and usually only found as cements and concretions, but in samples of this study it occurs quite commonly, although not in large concentrations (Boggs, 1992). Siderite is more common in the basin center than in the margin. In the basin center, siderite is present in over half of the samples (57 of 89 samples), with up to 6.7 wt%. In the basin margin, siderite occurs in 10 of the 28 samples, all at trace levels. Magnesite is found in only one sample in this study at 3.8 wt%, in the basin center. The rarest of the minor carbonates found in the GRF is kutnohorite (CaMn(CO₃)₂). Kutnohorite was identified in only one sample in the basin center John Savage 24-1 section, in stage S3, at only 0.7 wt%. It is likely to also occur as a minor phase in other samples, but only five John Savage 24-1 samples were checked for kutnohorite, in the subset specially analyzed with JADE software. Interestingly, this same sample also contained another rare mineral, woodhouseite (CaAl₃(SO₄)(PO₄)(OH)₆), which also was only identified using JADE.
Figure 4.20 SEM-EDS spectral patterns obtained in the basin center in the middle MU indicate high iron contents associated with carbonate minerals. No sulfur is present in these patterns, attributing iron to a carbonate mineral such as siderite or ferrodolomite. John Savage 24-1 samples clockwise from top left: JS-35, JS-45, and JS-71. Thin sections were coated in gold for SEM analysis, accounting for the Au peaks. Labels do not necessarily indicate the presence of a peak, but only where a peak would be expected for that element. Unlabeled peaks are secondary peaks of Ca or Fe.
4.5.4 Saline Minerals: Nahcolite, Dawsonite, Halite

All saline minerals in the GRF are sodium carbonates or bicarbonates, with the exception of halite (sodium chloride). The saline minerals include nahcolite (NaHCO$_3$) and dawsonite (NaAlCO$_3$(OH)$_2$) as major phases, and halite, natrite (Na$_2$CO$_3$), and northupite (Na$_3$Mg(CO$_3$)$_2$Cl) as minor phases. The minor phases natrite and northupite are combined with the major phase nahcolite in quantitative calculations for this study. The term “saline” is preferred to “subaqueous evaporite” because the origins of the minerals are still uncertain. The term subaqueous evaporite corresponds with the facies in which high quantities of saline minerals occur as described in Tänavsuu-Milkeviciene and Sarg (2012). The saline minerals are only common and abundant in the basin center sections, and are grouped by association of occurrence in the saline zone, which encompasses most of the middle MU. Saline minerals occur in 79 of the 89 basin center samples, and comprise 18 wt% of the samples on average. Only one sample in the basin margin contains halite, and only one sample contains nahcolite. Dawsonite was not found in any basin margin samples in even trace amounts.

Thick beds of saline minerals only occur in the middle MU in the basin center, as shown as dark purple (nahcolitic) and lavender subaqueous evaporite facies (halite dominated) in the stratigraphic column of the John Savage 24-1 and Shell 23X-2 sections shown in figures 3.2 and 4.7 by (Tänavsuu-Milkeviciene and Sarg 2012). Intervals of subaqueous evaporite rock types that were dominated by halite were not sampled for this study. Nahcolite occurs in many fewer samples than dawsonite, but in much higher quantities. Figure 4.21 shows comparative histograms of the frequency of nahcolite and dawsonite occurrences in basin center samples. Stratigraphic occurrences of nahcolite are highly punctuated with extreme concentrations; exhibiting an irregular, almost bimodal quantitative distribution. Dawsonite and halite have more continuous ranges of abundances (although this conclusion may be incomplete for halite due to the lack of samples taken from halite beds). Out of 89 samples, dawsonite occurs in 65, and halite in 41 samples. The maximum amount of dawsonite that occurs is 28 wt%. Nahcolite is present in only 34 samples, ten of which have over 60 wt%. 22 samples contain less than 6 wt% nahcolite and only two samples contain intermediate quantities of 24 and 26 wt%. These two samples are unique in that one sample spans two different distinctive beds in stage S2, and the other contains lenses of darker nahcolite in a fine grained matrix in upper stage S3. Therefore these two samples with 24 and 26 wt% may not be representative of true mineral proportions.
(Photos of these samples are included in Appendices E, H and I). Nahcolite is therefore a major phase primarily because it occurs in high quantities, whereas dawsonite is a major phase primarily due to its common occurrence in the basin center.

The uneven distribution of nahcolite is not expected to be an artifact of biased sampling, because the crystals are brown and not readily visually recognizable. Nahcolite-rich intervals can be mistaken for mudstone or even sandstone in hand samples, as it occurs in diverse crystal morphologies from microscopic clay-sized particles, to coarse grains and large nodules. Fine-grained intervals rich in nahcolite can be mistaken for organic-rich or clay-mineral-rich mudstone for its brown color. Samples that contain large quantities of nahcolite are usually poor in both clay minerals and organic matter. Therefore, XRD, or other mineral analysis, is especially important for rock type determinations of saline intervals. Supplemental File I has images of nahcolitic rich intervals.

Dawsonite is much less soluble than nahcolite, and is present in the leached portions of the basin center sections. Only empty vugs and other sedimentary structures are left as evidence that nahcolite was once present in the leached zone above stage S3 in the sections sampled. Therefore, XRD data provide an incomplete assessment of the distribution of nahcolite, which is no longer present just above the upper transition zone, above the point at which dawsonite has decreased. This may affect the understanding of nahcolite’s relationship to other minerals and conditions of formation. The appearance of nahcolite does not coincide with the stratigraphic disappearance or appearance of any other mineral, not even halite (Figures 4.7, 4.8).

Halite is the only major halide identified in this sample set, and northupite is the only minor mineral bearing chlorine. As previously noted, halite occurs as a major phase in the GRF, in some places forming nearly pure beds of halite, which were not sampled. Halite still occurs commonly as a minor phase in samples throughout the basin center section. In all but one sample which contained 11 wt% in this study, halite occurs in amounts of less than 1 wt%. Halite shows a discrepancy in results for the Shell 23X-2 core, between samples analyzed by ExxonMobil, and samples analyzed at Chevron. Halite was found in all 35 samples of the ExxonMobil Shell 3X-2 set, but in none of the 15 Chevron samples. Of the 39 samples from the John Savage 24-1 core (analyzed at Chevron), 7 samples contained halite. This may be due to the fact that samples with visible halite were intentionally not selected for the COSTAR set. Also, the XRD primary peak
used for identification of halite may have been obscured by the overlapping peaks of the internal standard zincite, used in the Chevron sample prep methods.

Northupite (Na$_3$Mg(CO$_3$)$_2$Cl) and natrite (Na$_2$CO$_3$), are both sodium carbonate saline minerals, which were only identified in one sample each, but in significant amounts of 21 and 16 wt% respectively. It is conceivable that natrite and northupite also occur in other saline samples in the basin center, but only five John Savage 24-1 samples were analyzed for these minerals separately using JADE software. In the sample containing 16 wt% natrite, nahcolite is 75 wt% of the sample, but in the sample with 21 wt% northupite, there is no nahcolite detected. Dawsonite does not co-occur in either sample with natrite or northupite. It has been suggested that the rare sodium carbonate phases may be alteration products of nahcolite, after exposure to ambient conditions during storage of the cores for many decades (Meurer, personal communication, 2010).

**Figure 4.21** Histograms of the frequencies of the two major saline mineral phases, showing the contrast in abundance distributions in the basin center (89 samples).
4.5.5 Accessory Minerals

Trace and uncommon phases in the GRF include sulfides, sulfates, phosphates, halides, oxides, and hydroxides, and one chain silicate. In general, each accessory mineral occurs at less than 2 wt% average, but maximum values may be up to 10 wt%. Therefore, confidence in their identification and quantification is low. It is possible that other accessory minerals are present in the GRF of the Piceance Basin in addition to those listed in table 4.1, but were not identified. Several accessory minerals were identified in the ExxonMobil Shell 23X-2 dataset from the USGS that were not found in the Chevron-analyzed COSTAR samples, and vice-versa. This difference can be attributed to different standards used for the two different analyses, and differences in interpretation methods. The ExxonMobil data identified two accessory minerals, anatase and barite, which were not found in any of the COSTAR samples. Accessory minerals that were identified in the COSTAR samples, but not in the ExxonMobil samples include anhydrite, gypsum, brucite, amphibole, woodhouseite, natrite, northupite and kutnohorite. The last four minor phases listed are from the COSTAR samples of the basin center John Savage 24-1 section, which were identified when interpreting results of five sample scans using JADE software. Woodhouseite was found in 2 samples, and natrite, northupite and kutnohorite were all identified in one sample each. They are potentially present in other samples, because the software was not programmed with standards for these rare minerals, and therefore could not recognize them in the other 77 samples. Future work should include reevaluation of all 82 samples using JADE software which has a more complete database of minerals.

Collectively, trace phases are more abundant in the basin center sections (ave. 2.8 wt %), than in the basin margin sections (ave. 1.4 wt%). This is partially attributable to halite being included in the “other” category, which occurs mainly in the basin center. An unidentified amphibole was detected in two samples in this study, one in the basin center, stage S3, at 0.6 wt%, and one in the basin margin; stage S5, at 2.0 wt%. Trace amphibole may be an indication of volcaniclastic contributions to the PCB (Surdam and Parker, 1972).

Sulfates are largely absent in the GRF, which is a distinguishing characteristic of many non-marine, evaporative basins (Eugster, 1980). Gypsum and anhydrite are more common in the basin margin than in the basin center. In the basin margin, anhydrite was found in five, and gypsum was found in seven of the 28 samples, at a maximum of 0.9 wt% and 2.0 wt%,
respectively. In the basin center, anhydrite was found in 8 samples, and gypsum in only 2 of the 89 samples, at a maximum of 2.1 and 0.6 wt%, respectively. Barite was identified in all 35 of the ExxonMobil Shell 23X-2 samples, but not found in any samples analyzed at Chevron. Sulfate minerals found in the basin margin are likely to be the results of weathering on the outcrops, and from post-drilling alteration of the core from the basin center. Barite in the ExxonMobil Shell 23X-2 dataset may reflect minor invasion of drilling fluid (Meurer, personal communication, 2010).

Pyrite is a common mineral, but is not abundant in the samples of this study. Pyrite has higher abundances in the basin center than in the margin. Pyrite was found in 34 of 35 ExxonMobil Shell 23X-2 samples, and in 47 of 54 Shell 23X-2 COSTAR samples. Pyrite occurs in the basin margin at an average of less than 1 wt%, with up to 6 wt% in stage S2. In the basin center, pyrite has an average of 1.7 wt%, with a maximum of 6.4 wt% in stage S1. Marcasite is also found to be present in 31 of the 35 Shell 23X-2 ExxonMobil samples, but was only identified in two of the COSTAR Shell 23X-2 samples, in none of the John Savage 24-1, and in only one of the Douglas Pass samples.

Apatite, Ca₅(PO₄)₃(OH,F,Cl), was identified as fluorapatite with Chevron’s software, and as apatite in the ExxonMobil dataset for the Shell 23X-2. All 35 occurrences of apatite in the basin center are from the Shell 23X-2 section, 29 of which were identified from the ExxonMobil samples. Fluorapatite was not recognized in any John Savage 24-1 samples. The maximum amount of apatite detected in the basin center is 8.8 wt%. In the margin, fluorapatite occurred in only one sample, but at a relatively high concentration of 5 wt%. In the CO-1 core, fluorapatite was identified in only one sample. (Robb and Smith, 1974). Woodhouseite, CaAl₃(SO₄)(PO₄)(OH)₆, was only identified in the basin center in two of the five samples evaluated using JADE software, and occurs in stage S3 at 1.4 and 2.9 wt%.

Anatase (TiO₂), was identified at trace levels in 34 of 89 samples in the basin center. All of these samples are in the Shell 23X-2 section. This is most likely an anomalous result attributed to differences in interpretation methods; since all 34 occurrences of anatase were detected in samples analyzed by ExxonMobil, and it was not detected in any of the samples analyzed by Chevron’s methods. Lack of detection may be attributed to low quantities of only 0.6 wt% maximum. Hydroxide minerals are extremely rare in this dataset, including Al (oxy-)
hydroxide, which occurs in the margin in one sample, and brucite (Mg(OH)$_2$) which was detected in one sample in the basin center.

4.5.6 Organic Matter

Organic matter in the basin margin ranges from 2 to 16 wt% s determined by XRD, and averages 7 wt%. Much higher concentrations exist in the basin center, where it ranges from 3 to 36 wt%, and averages 12 wt%. In the basin margin, organic matter quantities are less variable throughout the stratigraphic section than in the basin center, where quantities greatly fluctuate between intervals (Figures 4.3 and 4.4). The highest quantities of organic matter are found in the middle MU of the basin center, at 13.2 wt%. The middle MU also has the highest average quantities in the basin margin, but only 7.8 wt%. The thesis by Feng, 2011 includes the data for 225 samples analyzed by SRA from the same sections as used in this thesis. Supplemental File L includes quantitative results by two additional methods: total organic carbon (TOC) by source rock analysis (SRA), and organic carbon (Corg) by infrared spectroscopy (IR), for an expanded sample set including the same samples as analyzed by XRD.

4.6 Redox Indicators: V/Cr Ratio Proxy

The depositional environment responsible for the formation of so many rare minerals is of great interest, and geochemical proxies may be useful for understanding lake conditions during deposition. The ratio of vanadium to chromium is considered to be a proxy for redox conditions at the time of deposition, because the solubility of vanadium is sensitive to oxidizing and reducing conditions (Jones and Manning, 1994). Oxic conditions are indicated by a V/Cr ratio of less than 2, and anoxic conditions are indicated by a ratio of over 4.5. When the V/Cr ratio is between 2 and 4.5 conditions are considered to have been dysoxic during the time of sedimentation. Oxic conditions are defined as > 2.0 ml/l oxygen, and dysoxia is defined as between 0.0 to 2.0 ml/l (Jones and Manning, 1994). Feng (2011) also used geochemical proxies from inorganic chemical data from the U. S. Bureau of Mines 01A (USBM 01A) well in the Piceance basin to understand the depositional environment of the GRF. The USBM 01A well is close to the John Savage 24-1 well on the east edge of the halite depositional area of the basin center (Figure 2.2). The dataset from the USBM 01A section indicates that conditions were
already dysoxic to anoxic in the basin center in the initial lake stage S1, and mainly dysoxic throughout the rest of the lake’s history (Figure 4.22) (Feng, 2011).

In this study, V/Cr ratios were also analyzed for the Shell 23X-2 and John Savage 24-1 section in the basin center, which similarly indicate that anoxic conditions already existed early in stage S1 and continued into early stage S2. V/Cr ratios in the John Savage 24-1 well suggest that dysoxic conditions existed throughout most of the stratigraphic section of the basin center, with a few brief anoxic and oxic events during stage S3. Conditions appear to maintain a state of dysoxia or anoxia until stage S6, when oxic conditions are again indicated. Figure 4.23 shows depth plots of the V/Cr ratio for the basin center and margin sections. In the basin margin, Douglas Pass section, dysoxia is also indicated to have been the norm throughout all lake stages, with even fewer data points indicating the presence of oxic conditions. The basin margin also appears have experienced a very anoxic period early in the lower MU.

![Figure 4.22 Redox proxy depth plot from inorganic chemistry data for the USBM 01A well. A vanadium to chromium wt % ratio of less than 2 is indicative of oxic conditions, and over 4.5 indicates anoxic conditions. A V/Cr ratio between 2 and 4.5 indicates dysoxic conditions. Lake stages S1 through S6 are shown. Note that lake stage S1 is the most anoxic. (Jones and Manning, 1994). Modified from Feng, 2011.](image)
Figure 4.23 Depth plots of the redox proxy vanadium to chromium ratio for the basin center and basin margin locations. A V/Cr ratio of less than 2 is indicative of oxic conditions, and over 4.5 indicates anoxic conditions. A ratio between 2 and 4.5 indicates dysoxic conditions. Lake stages S1 through S6 are shown. Depth in feet on vertical axis. (Jones and Manning, 1994).

Ferrodolomite and buddingtonite both show depositional trends that approximate that of indicators of redox conditions on depth plots. The relationships are not quantitative and are stronger in some stratigraphic intervals than in others. The depth plot of ferrodolomite in the basin margin section, shown in figure 4.24, parallels the V/Cr ratio trend most strongly in the upper MU. A rough relationship between ferrodolomite and the redox condition proxy values is also apparent in the basin center, but is weaker than in the basin margin. Using the ratio of ferrodolomite to the sum of ferrodolomite and calcite, a correlation is apparent in the upper and
lower John Savage 24-1 MUs. No relationship between ferrodolomite and V/Cr values could be discerned for the Shell 23X-2 section.

A parallel trend is evident between anoxia indicators and quantities of buddingtonite in the basin center. The relationship is strongest when buddingtonite is plotted as a ratio to the sum of buddingtonite and potassium feldspar, but can also be discerned as a proportion of total feldspars. A marked decrease in buddingtonite near the top of rich zone R2, correlates with the change from an anoxic to more dysoxic environment at the lower transition, in the Shell 23X-2 section. A second decrease in buddingtonite is evident at R5, as a proportion to total feldspars in the John Savage 24-1 (Figure 4.25).

Figure 4.24 Parallel trends in the depth plots of the V/Cr proxy for redox conditions and the quantities of ferrodolomite are apparent in many stratigraphic intervals of the basin center John Savage 24-1 section (left, JS) and the basin margin Douglas Pass section (right, Margin DP). In general, when increasingly anoxic conditions are indicated, quantities of ferrodolomite also increase. Depth in feet and lake stages S1-S6 on vertical axis.
Figure 4.25 Parallel trends in depth plots of the proportions of buddingtonite to the sum of potassium feldspar and buddingtonite (left), and to total feldspars (center), and the V/Cr proxy for redox conditions in the basin center John Savage 24-1 (upper) and Shell 32X-2 (lower) sections. Changes in conditions from generally anoxic to generally dysoxic is indicated at the lower transition zone at R2 by parallel behavior between the redox indicator V/Cr and a decrease in the deposition of buddingtonite in the Shell 32X-2 section. Proportions of buddingtonite decrease at both R2 and R5. Depth in feet and lake stages S1-S6 shown on vertical axis.
4.7 Mineral Relationships

Robb and Smith (1974) report that in the CO-1 basin center section, many relationships exist amongst individual framework silicate minerals, as well as with several other mineral components, especially the saline minerals (Robb and Smith, 1974). Some of these trends in the CO-1 section can also be recognized in the John Savage 24-1, Shell 23X-2, and Douglas Pass data sets in this thesis. Relationships are strongest in the saline zone of the basin center, where authigenic minerals are in the highest proportions, and are weaker in the margin, where detrital dilution obscures patterns of authigenic deposition. In the CO-1 section, Fischer Assay oil yield data was used to estimate the volume of organic matter in relation to mineral quantities by Robb and Smith (1974). A direct positive relationship was reported between the abundance of organic matter and the peak heights of silicate minerals. Quartz, sodium feldspar, and potassium feldspar in particular exhibited strong relationships to organic matter concentrations in most stratigraphic sections, with coefficients of determination of 0.70 to 0.85 for all stratigraphic sections (Robb and Smith, 1974). The same relationship to silicate minerals has not been recognized in this dataset.

Only one quantitative relationship was identified in this thesis, between quartz and dawsonite, in the basin center. The correlation between the abundance of dawsonite and quartz is not strong when compared across the entire stratigraphic section, but when the interval is limited to the middle MU, the positive relationship becomes strong ($R^2 = 0.85$) (Figure 4.26). This is the strongest positive relationship found in this study between any of the detected minerals.

Many minerals in this thesis exhibit relationships that are described as “limited exclusive.” Limited exclusive relationships are defined as two minerals that are nearly mutually exclusive to each other, so one mineral is present only in minor quantities when the other is abundant. Coexistence between many major phases with limited exclusive relationships appears to be contingent on one mineral being present at less than 6 wt%. Another set of limited exclusive relationships involve minerals which do not coexist at over approximately 11 wt%. Limited exclusive relationships may indicate that one mineral is degraded or altered before the other mineral will form; or that a more direct parent-daughter relationship between authigenic phases exists. Alternatively, a dilution effect may be indicated, from one mineral rapidly precipitating in large quantities at the expense of all other phases still depositing at normal rates.
In most cases, it is interpreted that limited exclusive relationship represents two minerals that require separate geochemical conditions in order to form or be preserved, with a small overlap in the range of conditions that each mineral exists.

**Figure 4.26** Quantitative positive correlation between dawsonite and quartz in the basin center, restricted to stages S2 and S3 only (middle mineral unit), basin center Shell 23X-2 and John Savage 24-1 sections.

Only one *perfectly* mutually exclusive relationship was found in this thesis, between nahcolite and analcime, as no samples have been identified that contains both minerals (Figure 4.28). Nahcolite, and the other minor sodium carbonate minerals, northupite and natrite, also exhibit the highest number of limited exclusive relationships with other major mineral phases. Nahcolite only coexists in the same sample if one mineral or the other is present at 6 wt% or less. This is true for dawsonite, buddingtonite, plagioclase and dioctahedral 2:1 clays, as shown in figure 4.27. These relationships are likely to be partially due to the extreme distribution of nahcolite in the basin. Nahcolite primarily deposited only in the saline zone of the basin center middle MU, whereas analcime only occurs in significant amounts in the basin margin where nahcolite is very rare (Figure 4.28). Illite-smectite-mixed I/S clay minerals also primarily deposited in the basin margin and lower MU of the basin center (Figures 4.3 and 4.4). Nahcolite deposition in the saline zone commonly occurred as a surge of precipitation that largely overwhelmed the normal clastic and chemical sedimentary fluxes in the basin center. The relationships between nahcolite and other minerals likely reflect the dilution effect of these
Halite shows no clear quantitative relationship to the other major saline minerals, but it does co-occur with nahcolite in the same stratigraphic intervals. The sample containing the most halite (11 wt%) also contains 2 wt% dawsonite, and 68 wt% nahcolite.

Figure 4.27 The relationship of several major phases with nahcolite is limited exclusive, as shown in plots from the basin center sections. Neither mineral occurs at over 6 wt% in any sample where the other is also present. The relationship is similar for dioctahedral 2:1 clays (illite-smectite), buddingtonite, dawsonite and plagioclase (albite). Natrite and northupite are combined with quantities of nahcolite.

The distribution of analcime across the PCB opposes that of the saline minerals, nahcolite, dawsonite, and halite as well as that of buddingtonite. This contributes to the limited exclusive relationship that analcime exhibits with dawsonite and buddingtonite, which have the highest abundances in the saline middle MU of the basin center, and don’t coexist with analcime at over 6 wt% (Figure 4.28).

In the CO-1 core, calcite and analcime have parallel occurrences which oppose that of dawsonite and nahcolite, as observed by Robb and Smith (1974). The common depositional patterns of calcite and analcime are also recognizable in this thesis in both the basin margin and
basin center sections. Robb and Smith noted that calcite and analcime are both most abundant where clastic influx is high, which has been confirmed in this thesis (Robb and Smith, 1974). Figure 4.11 shows that the highest deposition of elemental calcium also occurs in the fresher intervals of the basin center in the lower and upper MUs. Although analcime and calcite do occur in similar stratigraphic and basin locations, a limited exclusive relationship is exhibited between analcime and calcite, at quantities below 11 wt% (Figure 4.28).

**Figure 4.28** Analcime demonstrates a perfectly mutually exclusive relationship with the saline mineral, nahcolite. Analcime exhibits a nearly exclusive relationship with the phases buddingtonite and dawsonite in basin center Shell 23x-2 and John Savage 24-1 sections. A negative relationship is apparent between analcime and calcite in both the margin and basin center sections, showing that except for one outlier, no sample contains over 11 weight per cent calcite if analcime is also present at over 11 weight per cent.

Both dawsonite and buddingtonite share similar relationships to analcime, nahcolite, clay minerals, and calcite (Figures 4.27, 4.28, 4.29, 4.30 and 4.31). Dawsonite shares parallel stratigraphic occurrences with buddingtonite, but discernible positive quantitative relationship
between the two minerals could not be found in this study (Figures 4.7, 4.9). Limited exclusivity relationships between calcite and dawsonite, which don’t co-occur above 6 wt%, and calcite and buddingtonite, which don’t co-occur above 11 wt%, were predicted from the basin distributions and relationships with other minerals (Figure 4.30). Supplemental File M illustrates qualitative relationships on depth plots between and amongst buddingtonite, dawsonite, plagioclase, potassium feldspar, and quartz.

**Figure 4.29** Cross plot correlations of total clay minerals versus buddingtonite (top), and dioctahedral 2:1 clay minerals versus the sum of buddingtonite and dawsonite (bottom) in the basin center and basin margin. Semi-mutually exclusive relationships show co-occurrence between minerals is limited to both phases being below 10 weight per cent. These suggest that there is a relationship between the breakdown of clay minerals and formation of authigenic phases.
Figure 4.30 Limited exclusive relationships between dawsonite and calcite, and buddingtonite and calcite which were predicted by the theory that calcite forms and is preserved in a different set of conditions than minerals which are abundant in the saline zone of the basin center. With the exception of one outlier, calcite and dawsonite do not co-exist in the same sample at over 6 wt%. Buddingtonite and calcite do not co-occur at over 11 wt%.

In samples containing dawsonite, clay minerals rarely occur at over 10 wt% (Figure 4.31A). An authigenic mineral relationship is suggested to be present by the demonstration that the sum of potassium feldspar and dawsonite also have a limited exclusive relationship with the dioctahedral 2:1 clay minerals. (Figure 4.31C). This relationship is also present for the sum of dawsonite and plagioclase (Figure 4.31B).

Clay minerals and feldspars usually do not coexist unless one or the other is present at less than 11 wt% (Figure 4.32). This trend is true in the basin center for dioctahedral 2:1 clay minerals versus potassium feldspar, and plagioclase, and also holds for kaolinite and potassium feldspar in the margin. When illite-smectite clay minerals are present in a sample at over 12 wt% in the basin center, plagioclase does not occur at over 10 wt%, and potassium feldspar is never present at over 6 wt%. In the margin, when potassium feldspar is present at over 11 wt% in a
sample, kaolinite does not occur at over 2 wt%. The differences in the clay mineral to feldspar relationship between locations is likely attributable to the higher detrital contributions in the margin, versus higher authigenic proportions in the basin center.

Figure 4.31 Limited exclusive relationships, save one or two outlying points, between total clay minerals and A) dawsonite, B) dawsonite+plagioclase, and C) dawsonite+ potassium feldspar in the basin center, with co-occurrence of minerals at less than 10 to 15 weight %.
Aragonite and dolomite were reported to have an inverse relationship in the Mahogany zone of the CO-1, but aragonite showed no relationship with calcite (Robb and Smith, 1974). This relationship could not be reproduced from data in this thesis. Siderite tends to roughly co-occur in the same stratigraphic intervals as high concentrations of ferrodolomite (Figure 4.6).

![Graphs showing relationships between feldspar and clay mineral members.](image)

**Figure 4.32** Relationship between individual feldspar and clay mineral members. Plagioclase feldspar vs. illite-smectite, potassium feldspar vs. illite-smectite in the basin center, and potassium feldspar vs. kaolinite in the margin. All exhibit a limited exclusive relationship with cut-offs at roughly 5 to 10 wt%.

A relationship is suspected between buddingtonite and organic matter since the authigenic phase would require a source of nitrogen for formation. A non-quantitative positive trend does exist in the middle MU when using data from the infrared method for organic matter (as opposed to using organic matter concentrations determined by XRD) (Figure 4.33). The quantities of organic matter and buddingtonite are not proportional and therefore do not have high coefficients of determination, but their concentrations do covary positively. Buddingtonite and organic matter do not track as well in the upper or lower MUs, but this can be attributed to the fact that buddingtonite is less abundant in these stages.
Figure 4.33 Relationship between buddingtonite and organic matter in the basin center, showing a positive, non-quantitative correlation that is strongest in the middle mineral unit (saline zone) of the John Savage 24-1 section. Basin Center, 54 samples, infrared organic matter determination. Depth in feet on vertical axis.

In most published values for quartz and feldspar in mudstones, the quartz to feldspar ratio is greater than 2:1 (Boak et al. 2012). In the GRF, the quartz to feldspar ratio is well below two throughout most of the stratigraphic sections in both basin locations (Figure 4.34). The ratio of quartz to feldspar is above two only in lake stage S1 in both the margin and basin center, with a maximum of seven in the basin center Shell 23X-2 section.
Figure 4.34 Ratio of quartz to total feldspars in the basin center John Savage 24-1 and Shell 23X-2 sections, and in the margin, Douglas Pass section. Quartz: feldspar ratio is over 2 in stage S1 in both the basin center and margin. The ratio is less than two from stage S2 to the top of the GRF formation in both basin locations, except for a spike in S3 in the basin center. Depth in feet on vertical axis.

Analcime and plagioclase are the two primary sodium-bearing minerals in the basin margin section, as both minerals are sodium aluminum silicates. As shown in depth plots in figure 4.35, Na/Al ratios are very stable throughout the margin section, even when sodium concentrations increase, which are paralleled by increases in analcime formation, but not necessarily by increases in sodium feldspar. Na/Al ratios in the basin margin averaged only 0.19 with a maximum of 0.39. In contrast, figure 4.36 shows that Na/Al ratios vary greatly in the
basin center, with an average of 2.94 in this sample set, and a maximum of 55.7, where increases in sodium concentrations are paralleled by increases in nahcolite deposition, NaHCO₃.

Nahcolite, dawsonite and plagioclase are the main sodium-bearing minerals in the basin center. Just as analcime correlates with elemental sodium in the basin margin samples, nahcolite and elemental sodium concentrations correlate in the basin center (Figure 4.35). Nahcolite concentrations track closely with the ratio Na/Al on a depth plot in the basin center sections (Figure 4.36). Dawsonite shows a weak negative correlation with Na₂O quantities, whereas plagioclase shows no discernible correlation to sodium concentrations in the basin center.

Sodium is normalized to aluminum to account for the sodium which occurs in silicate minerals. High sodium concentrations in the basin center appears to have occurred independently of aluminosilicate minerals, and extreme, punctuated increases in sodium concentrations occurred in the middle MU, without corresponding increases in aluminum concentrations.

**Figure 4.35** Quantities of elemental sodium and Na/Al versus sodium-bearing minerals in the basin margin. The sum of plagioclase and analcime gives a curve that is identical to the Na₂O curve. Sodium is in per cent, as an oxide as detected by ICP in percent of total major ions. Sodium to aluminum ratio, in dimensionless units, demonstrates that aluminum concentrations were over twice that of sodium concentrations throughout the lake history in the basin margin. Depth in feet on vertical axis.
Figure 4.36 Na/Al and Na$_2$O versus quantities of major sodium-bearing minerals in the basin center sections, John Savage 24-1 and Shell 23X-2. Nahcolite strongly correlates with Na/Al ratios. Sodium is normalized by aluminum to account for sodium in silicate minerals. Vertical axes are in feet, horizontal axes are in weight per cent for minerals, and dimensionless for the ratio of Na/Al. Sodium is in per cent, as an oxide as detected by ICP in percent of total major ions.
Changes in the silicon to aluminum ratio are related to the abundance of both analcime and quartz in the basin margin (Figure 4.37). As a low-silicon aluminosilicate, the chemical formula of analcime, NaAlSi$_2$O$_6$·H$_2$O, has a Si/(Na+Al) ratio of 2:1, but can vary between 2 and 3 in sedimentary analcimes. Other major framework silicates identified have a ratio of 3:1, in the case of sodic and potassic feldspars (Deer et al., 1992). Analcime shows an inverse, non-quantitative trend with quartz on a depth plot in the basin margin. Quartz parallels the variations in the Si:Al ratio with depth. Therefore, when Si/Al is low, quartz concentrations are also low, whereas analcime quantities are high. The depth trends indicate that Si availability is a control on the formation of authigenic framework silicate minerals, such as analcime. In contrast to the basin margin, only a very weak positive relationship can be found between SiO$_2$ and quartz in the basin center, and no relationship between Si/Al and quartz can be identified.

Figure 4.37 Depth plots from the Douglas Pass basin margin sections comparing the ratio of silica to alumina, vs. abundance of quartz and analcime. Si/Al = SiO$_2$/Al$_2$O$_3$. These plots demonstrate the relationship between Si availability and the formation of authigenic framework silicate minerals, quartz and analcime. Depth in feet on vertical axis.
4.8 Rock Types

Most rock types of the GRF are fine-grained, and may be composed of a combination of chemical sedimentary phases, authigenic and detrital phases. Samples in the basin margin include fine sandstone, siltstone, mudstone and marlstone. Samples from the basin center include siltstone, mudstone, marlstone, and saline subaqueous evaporite. Combination of grain size with mineral data produces a wider variety of rock types than is generally reserved for clastic sedimentary rock. Mixed carbonate and siliciclastic sediments are not abundant in the rock record, and require a classification scheme that combines both sandstone and limestone nomenclature (Boggs, 1992).

4.8.1 Rock Type Classification

The large set of minerals identified from the GRF in this study results in a diverse set of rock types beyond the scope of most standard classifications. The classification used in this thesis is a combination of traditional sedimentary rock type schemes modified from Pettijohn (1957) and Picard (1971). Rock types are defined using a series of graphic ternary plots to incorporate all four major classes of mineral constituents present: Ca-Mg-Fe carbonate minerals, framework silicates, clay minerals, and saline minerals. Analcime, nahcolite, and dawsonite are given special weight in this classification, independent of their respective mineral categories, to emphasize their individual volumetric importance. All 117 samples are included on each ternary plot, grouped by basin location into 3 categories: basin margin, upper basin center and lower basin center. The basin center samples are divided into two stratigraphic intervals to illustrate contrasts in mineral compositions, and similarities between the lower basin center and basin margin sample sets. The “lower basin center” corresponds with the lower mineral unit below the lower transition zone. Table 4.4 lists the terms used to describe the complete array of rock types present, and the mineral quantities that define them.

After grain size, the first major mineral criterion used to name and classify rock types is the abundance of Ca-Mg-Fe carbonate minerals. Pettijohn (1957) defines a marlstone as a mudstone with 35%-65% calcium carbonate content. Fe-rich dolomite is the predominant Ca-Mg-Fe carbonate mineral over calcite in the majority of the samples represented in this study. Therefore, the term marlstone may be broadened here to include dolomitic mudstone samples with subequal portions of Ca-Mg-Fe carbonate and silicate minerals. For this study, “marlstone”
### Table 4.4 Rock type modifier terminology as determined by a classification scheme based on mineralogy and superimposed upon grain size divisions.

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Mudstone</td>
<td>Mean grain size in clay range</td>
</tr>
<tr>
<td>Siltstone</td>
<td>Mean grain size in silt range</td>
</tr>
<tr>
<td>Sandstone</td>
<td>Mean grain size in sand range</td>
</tr>
<tr>
<td>Marlstone</td>
<td>Mudstone with Carb/(Carb + Clay + Qtz + Fsp) &gt; 1/3 and &lt; 2/3</td>
</tr>
<tr>
<td>Marly Siltstone/Sandstone</td>
<td>Siltstone/Sandstone with Carb/(Carb + Clay + Qtz + Fsp) &gt; 1/3 and &lt; 2/3</td>
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<tr>
<td>Calcareous/Dolomitic Mudstone</td>
<td>Mudstone with Carb/(Carb + Clay + Qtz + Fsp) ≥ 2/3</td>
</tr>
<tr>
<td>Subaqueous Evaporite</td>
<td>Saline/(Saline + Carb + Clay + Qtz + Fsp) &gt; 1/2</td>
</tr>
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<table>
<thead>
<tr>
<th>Mineral Modifier</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>Argillaceous</td>
<td>Clay/(Clay + Qtz + Fsp) &gt; 1/2</td>
</tr>
<tr>
<td>Siliceous</td>
<td>(Qtz + Fsp)/(Clay + Qtz + Fsp) &gt; 1/2 and Qtz/(Qtz + Fsp) ≥ 3/4</td>
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<tr>
<td>Feldspathic</td>
<td>(Qtz + Fsp)/(Clay + Qtz + Fsp) &gt; 1/2 and Qtz/(Qtz + Fsp) &lt; 3/4</td>
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<tr>
<td>Zeolitic</td>
<td>Analcime/(Carb + Clay + Qtz + Fsp + Analcime) ≥ 1/10</td>
</tr>
<tr>
<td>Saline</td>
<td>Saline/(Saline + Carb + Clay + Qtz + Fsp) &gt; 1/10</td>
</tr>
</tbody>
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**Abbreviations used:**

- **Carb:** Divalent carbonate minerals including Fe-dolomite, calcite, aragonite, Mg-calcite, siderite, Mg-siderite, magnesite, kutnohorite
- **Clay:** Clay minerals including illite, mixed layer illite-smectite, smectite, muscovite, trioctahedral clay, chlorite, kaolinite
- **Qtz:** Quartz
- **Fsp:** Feldspar minerals including albite, potassium feldspar, and buddingtonite
- **Saline:** Sodium salts including nahcolite, dawsonite, halite, natrite, northupite

is used to describe a class of mudstone, and “marly” is used to describe classes of sandstone, siltstone or saline subaqueous evaporite samples, in which the proportions of Ca-Mg-Fe carbonate minerals is between 1/3 and 2/3, as a ratio to other major mineral classes. This is illustrated in a ternary plot with end members of Ca-Mg-Fe carbonate minerals, total clay minerals and silicate minerals as in figure 4.38 (Boak et al. 2012; Pettijohn, 1957). No limestone or dolostone rock types were sampled for this thesis, so all samples consist of less than 2/3 total Ca-Mg-Fe carbonate minerals. Ca-Mg-Fe carbonate minerals in this study combined to comprise the “carbonate minerals” end member include ferrodolomite, calcite, aragonite, Mg-calcite, siderite, Mg-siderite, magnesite, and kutnohorite as noted at the bottom of table 4.4.
Figure 4.38 Ternary plot illustrating the first main criterion for rock type classification: Ca-Mg-Fe carbonate mineral abundance. This plot is used to designate which samples are termed “marlstone” or “marly” (>1/3 wt% Ca-Mg-Fe carbonate minerals); “siliceous,” “feldspathic” or “arkosic” (<1/3 wt% Ca-Mg-Fe carbonate minerals), or “argillaceous” (clay minerals > quartz + feldspar). All 117 samples are plotted here, designated by basin location (basin margin vs basin center), and upper and lower basin center to show the similarities between basin margin and lower basin center samples. Modified after Boak et al. 2012.

Clay mineral abundance is the second main mineral criterion used to classify rock types. Argillaceous rock types are defined as samples which contain more clay minerals than quartz and feldspar, with respect to the same ternary plot in figure 4.38 (Picard, 1971). The “clay minerals” end member of the ternary plot includes all sheet silicate minerals, and the “Quartz + Feldspar” end member includes plagioclase, potassium feldspar, buddingtonite, and quartz, but not analcime. Samples which have less clay minerals than quartz plus feldspar are termed siliceous, feldspathic (mudstone), or arkosic (sand or siltstone).

The third criterion used in rock type classification of samples in this study is based on silicate mineral abundance and type: quartz-rich or feldspar-rich. Rocks of the GRF contain high concentrations of feldspar minerals. Results show that all but one of the sandstone and siltstone
samples in this study are arkosic, and the majority of mudstone and marlstone samples are feldspathic. The most common definition of arkose is a sandstone with over 20 to 30% feldspar minerals, and more feldspar than rock fragments (Boggs, 1992). This definition has been adapted for this study to define samples of any grain size with over 25% total feldspar minerals with respect to clay minerals and quartz, as either arkosic (sandstone or siltstone) or feldspathic (mudstone or marlstone), as shown in the ternary plot in figure 4.39. Conversely, samples with less than 25 wt% total feldspars \[
\text{feldspar}/(\text{feldspar} + \text{Quartz} + \text{clay}) < 1/4
\] with respect to the same ternary plot are defined as siliceous. Rock fragments were not quantified in this study due

![Ternary plot](image)

**Figure 4.39** Ternary plot illustrating the second and third criteria used for rock type classification in this study: relative abundances of silicate and sheet silicate minerals. This plot defines which samples are termed “feldspathic” or “arkosic” (>25 wt% feldspars relative to quartz and clay minerals), “siliceous” (<25 wt% feldspars relative to quartz and clay minerals), or “argillaceous” (>50 wt% clay mineral relative to feldspar and quartz content). All 117 samples are plotted here, designated by basin location (basin margin vs. basin center), and upper and lower basin center to show the similarities between basin margin and lower basin center sample sets. Note how lower basin center samples have much lower feldspar content than upper basin center samples. Lower basin center and basin margin samples are the most rich in clay minerals. Modified after Boak et al. 2012.
to the fine-grained nature of most rock types. Most rock fragments identified in core are rip-up clasts of mud in the brecciated oil shale facies types (Tänavsuu-Milkeviciene and Sarg, 2012).

The last main criterion used for defining rock types addresses the saline mineral component. Subaqueous evaporite rock types are defined as samples composed of greater than 50% total saline minerals, relative to Ca-Mg-Fe carbonate minerals and silicate + clay mineral end members, as shown in the ternary plot in figure 4.40. The term “subaqueous evaporite” corresponds with facies defined by Tänavsuu-Milkeviciene and Sarg (2012) in their stratigraphic study of the GRF of the PCB using the same core sections as in this thesis. Saline minerals include nahcolite, halite, dawsonite, natrite, and northupite as listed in Table 4.4. Samples with less than 50%, but over 10% Saline/(Saline + Carb + Clay + Qtz + Fsp) minerals are termed

![Ternary plot illustrating the fourth main criterion used for rock type classification in this study: relative abundance of saline minerals. This plot defines which samples are termed “saline,” (>10 wt% saline minerals, relative to Ca-Mg-Fe carbonate and silicate minerals), or “subaqueous evaporite” (>50 wt% saline minerals, relative to Ca-Mg-Fe carbonate minerals and silicate minerals). All 117 samples are plotted here, designated by basin location (basin margin vs. basin center), and upper and lower basin center to show the similarities between basin margin and lower basin center sample sets. Only the upper basin center samples contain saline or subaqueous evaporite rock types. Modified after Boak et al. 2012.](image.png)
“saline,” or are identified by the dominant saline mineral (Table 4.4). When a sample has over 10% dawsonite, or over 10% nahcolite/(Saline + Carb + Clay + Qtz + Fsp), “saline” is replaced with “dawsonitic” or “nahcolitic.”

Results show that all saline subaqueous evaporite rock type samples are nahcolitic, whereas most samples which are “saline” are “dawsonitic”. Saline and subaqueous evaporite rock types are present only in the basin center section, specifically in the saline zone in lake stages S2 and S3 (middle MU). Intervals of the John Savage 24-1 and Shell 23X-2 cores which were visually dominantly halite were not sampled, so “halitic” is not necessary to describe this dataset (Boak et al. 2012).

In addition to the four major component classes used in rock type classification, high proportions of zeolite minerals are noted using the modifier “zeolitic” for samples with over 10 wt% analcime relative to Ca-Mg-Fe carbonate minerals and silicate minerals (Figure 4.41).

![Figure 4.41 Ternary plot illustrating the criterion to define “zeolitic” rock types. “Zeolitic” samples are >10 wt% analcime, relative to Ca-Mg-Fe carbonate minerals and silicate and sheet silicate mineral end members. All 117 samples are plotted, designated by basin location (basin margin vs. basin center), and divided by upper and lower basin center to show the similarities between basin margin and lower basin center sample sets. Only the basin margin samples contain zeolitic rock types. Modified after Boak et al. 2012.](image-url)
Results show that in contrast to saline and subaqueous evaporite rock types, all zeolitic rock type samples are found in the margin, and none are found in the basin center (Figure 4.41).

4.8.2 Rock Types in Basin Margin vs. Basin Center Locations

Samples in the basin margin consist of relatively even portions of the four main rock types present. Basin margin rock types include seven sandstone, five siltstone, eight siliceous mudstone, and eight marlstone samples (Figure 4.42). Limestone is known to be a prevalent rock type in the basin margin, but these are not represented in the samples in this study (Suriamin, 2010; Tännavsuu-Milkeviciene and Sarg 2012). As defined by the previous four ternary plots (Figures 4.38, 4.39, 4.40, 4.41), all of the siltstone samples in the basin margin are arkosic, and all but one of the sandstone samples are arkosic. Twenty-three out of all twenty-eight basin margin samples are classified as feldspathic or arkosic, and only five samples are siliceous. Six samples are argillaceous, and eleven samples are zeolitic. There are no subaqueous evaporite or saline samples in the basin margin.

Samples are less evenly portioned in the basin center than in the basin margin, with the great majority of rock types being mudstone. Only two of eighty-nine samples from the basin center sections are siltstone, and ten samples are saline subaqueous evaporite. The other 78 samples are all mudstones by grain size, and 44 of those are marlstones (Figure 4.43) Sandstone does exist as a minor rock type in the basin center, but isn’t represented by any of the samples selected for this thesis.

Fifty of the 89 basin center samples are composed of over 1/3 Ca-Mg-Fe carbonate minerals (with respect to quartz, feldspar and clay minerals) of which six are “marly” subaqueous evaporite or siltstone samples (Figure 4.38). Like the basin margin samples, the majority of basin center samples are arkosic or feldspathic. Sixty-nine samples are feldspathic or arkosic, and only 20 samples are siliceous. Both basin center siltstone samples are arkosic, and one is marly (Figures 4.38 and 4.39). Ten samples are argillaceous, but no samples are zeolitic (Figures 4.39 and 4.41). Forty-nine samples are saline or subaqueous evaporite, including 35 dawsonitic, and 13 nahcolitic samples (Figure 4.40). Table 4.5 lists all rock types by basin location, and gives the number of samples of each rock type identified. Supplemental File N lists the rock type description for each sample and the end member proportions used to classify each sample.
Volcaniclastic rock is abundant in the PCB, and has been identified in the sections analyzed in this study, according to core descriptions by Tänavsuu-Milkeviciene and Sarg (2012). A single tuff sample was included in this study, and has been determined to be a dawsonitic feldspathic mudstone. Tuff is often composed of highly reactive or unstable minerals, and tuffs in the GRF of Wyoming are reported to contain traces of hornblende and pyroxene (Surdam and Parker, 1972). Two samples with trace amounts of amphibole were identified amongst those in this study of the GRF of the PCB, one from the basin margin in stage S5, and the other from the basin center in lower stage S3, which may represent remnants of volcanic ash contribution to the PCB. The tuff sample in this study came from the basin center saline zone of lake stage S3 in the middle MU of the John Savage 24-1 section, and is composed primarily of
quartz, potassium feldspar, buddingtonite, and dawsonite, with less than 10 wt% each of ferrodolomite and clay minerals. No amphibole was detected in this sample, and neither does the tuff sample contain any analcime, which is proposed in the literature to be formed from volcanic sediments (Surdam and Parker, 1972; Deer et al. 1992).

Figure 4.43 Photomicrographs of rock types in the basin center, John Savage 24-1: A) Nahcolitic Feldspathic Subaqueous Evaporite, ppl. B) Feldspathic Mudstone, ppl. C) Half Nahcolitic Subaqueous Evaporite, Half Feldspathic Mudstone, ppl. D) Dawsonitic Feldspathic Mudstone, xpl. All 4x magnification, stage S3, John Savage 24-1. Siltstone and marlstone rock types of the basin center are not pictured.
Table 4.5 Number of samples of each grain size and rock type in this thesis, by location in the basin. Samples correspond to data points on ternary plots in previous figures, and definitions of nomenclature used are explained in Table 4.4. *Two basin center samples contain two different rock types, because the samples span two distinct beds. Therefore the total number of rock types is two more than the total number of samples.

<table>
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<th>Location</th>
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<td>SUM Total Basin Center</td>
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4.8.3 Mineralogy of Rock Types by Grain Size

Sandstone samples from the GRF (only represented in the basin margin sections) are rich in quartz, plagioclase and K-feldspars, analcime and clay minerals. Notably, no sandstone samples contain buddingtonite, despite the fact that they are very feldspar rich. Sandstone samples contain the most Na-K-Ca feldspars of any other rock type in the basin margin, and the highest average abundance of quartz of any other rock type in either the basin margin or basin center. Sandstone samples are also unique in the GRF because they contain up to 37 wt% analcime and up to 35 wt% clay minerals. Table 4.6 summarizes the mineral composition of each rock type grain size in the basin margin and basin center.

Siltstone samples are composed primarily of feldspars, clay minerals, and analcime in the basin margin, whereas siltstone samples in the basin center are primarily plagioclase, potassium feldspar, and dolomite. Of all rock types, siltstone samples are the richest in analcime in both the basin margin and basin center, with an average of 17.7 wt% in the basin margin, twice as high as the average analcime content in sandstone samples (8.8 wt%). Siltstone is also the richest of all rock types in feldspars. Siltstone samples in the basin center are even more feldspar rich than basin margin siltstone and sandstone, with an average of 51 % Na-K-Ca feldspars.

Mudstone samples are rich in feldspars, clay minerals, organic matter, and analcime in the basin margin. In the basin center, feldspars, clay minerals, quartz, ferrodolomite, buddingtonite, and dawsonite all occur in significant amounts in mudstone. Mudstone samples have the highest occurrences of buddingtonite (11 wt% average in the basin center), and the most clay minerals (average of 34 wt% in the basin margin, and18 wt% in the basin center), of any rock type. The highest amounts of buddingtonite, and the highest amounts of Na-K-Ca feldspars do not occur in the same set of rock type samples. Mudstone samples also have the highest concentrations of quartz of any rock type in the basin center, above that of siltstone, with up to 43 wt%. Saline minerals occur at high levels in mudstone samples, with up to 28 wt% dawsonite in the basin center.

Marlstone samples are ferrodolomite and calcite rich by definition, but notably, siderite is not found at its highest quantities in marlstone samples, but in mudstone samples at 6.7 wt% max, which suggests it may be a later diagenetic phase. This could be evidence that that siderite exists as a cement or matrix component rather than as a framework grain. The abundance of
ferrodolomite is comparable in marlstone samples of the basin margin and the basin center. By contrast, calcite averages are four times greater in marlstone of the basin margin. Marlstone samples contain the highest maximum amounts of plagioclase and potassium feldspars, (as opposed to the highest average concentrations) in the basin center. Buddingtonite quantities are also high in marlstone samples of the basin center. Notably, dawsonite occurs in its highest abundance in marlstone samples, at 9 wt% average. By comparison, dawsonite only occurs at 3 wt% average in subaqueous evaporite samples.

Subaqueous evaporite samples, which are found only in the basin center, are dominated by saline minerals by definition, but this is only true for nahcolite and halite. Dawsonite occurs in relatively low levels in subaqueous evaporite samples, compared to marlstone and mudstone samples. Subaqueous evaporite samples have the lowest abundances of all silicate and Ca-Mg-Fe carbonate minerals of all rock types, due to nahcolite being the dominant phase in every sample with an average of 76%.
Table 4.6 Average and maximum mineral quantities by grain size rock type in weight % by basin location. Pink cells with red text show conditional formatting for values in the top 10%, to highlight the dominant minerals of each category. Note that a category of grain size in the basin margin may not contain the same dominant mineral abundances as in the basin center. Values are normalized to 100% on an organic matter-free basis for the basin center.

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<tr>
<th>Margin Rock Types</th>
<th>Quartz</th>
<th>Plagioclase</th>
<th>K-feldspar</th>
<th>Buddingtonite</th>
<th>Common Feldspar</th>
<th>Analcime</th>
<th>Calcite</th>
<th>Aragonite</th>
<th>Dolomite + Ankerite</th>
<th>Siderite</th>
<th>Nahcolite</th>
<th>Other Clays</th>
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CHAPTER 5
DISCUSSION

The unique mineral assemblages present in the Green River Formation (GRF) are a distinguishing characteristic of these fine-grained, organic-rich lacustrine sediments (Table 4.1). An unusually wide range of minerals was made possible in the GRF due to the decomposition of organic matter and detrital minerals under extreme conditions of high alkalinity and low redox potential. The subsequent availability of abundant carbon, nitrogen, and high salinity, allowed for the formation of large quantities of authigenic minerals. The resulting assemblages are a consequence of both clastic and chemical contributions to a restricted basin compartmentalized by an established stratified water column. The conditions indicated by the mineral assemblages of the GRF may serve as an extreme model of more moderate processes which commonly take place in many restricted basin environments. Therefore, interpretation of the GRF as an end member analog may be applied to other organic rich formations containing more subtle mineralogic gauges of depositional trends (Demaison, 1980; Dyni, 1996, 1998).

5.1 Authigenic Minerals and Their Distribution

Many authors, including Milton (1956, 1971), Robb and Smith (1974) and Desborough (1978) have suggested that the majority of minerals of the GRF in the PCB are of authigenic origins. Evidence in this thesis verifies that a large proportion of the mineral assemblage is authigenic, but that detrital minerals still comprise significant contributions to the basin sediments, especially at the basin margin. Evidence that a large proportion of feldspars and other aluminosilicates in the GRF of the PCB are authigenic includes the detection of very pure compositions, and very fine-grained, euhedral crystals by SEM - EDS (Figures 4.12, 4.13, and 4.16).

The next logical question raised is: which minerals are of authigenic origins, and which were the original clastic precursors to the authigenic minerals. The detrital components to the paleobasin are best represented by the assemblage that deposited at the base of the GRF stratigraphic section in an incipient lake, when waters were still fresh to brackish, and before a stratified water column had become well-established, or high degrees of alteration had begun.
This mineral assemblage is from the rich zone R0, at the base of the lower mineral unit (MU), and generally consists chiefly of quartz, clay and carbonate minerals (Figures 4.1, 4.2, Table 4.3) (LaClair and Lowenstein, 2009; Tänavsuu-Milkeviciene and Sarg, 2012).

In the basin margin, the major minerals in rich zone R0 are quartz, smectite and kaolinite clay minerals, and plagioclase and potassium feldspars (Figure 4.3). In the basin center, the major minerals of R0 are quartz, illite or muscovite clay minerals, plagioclase, calcite and ferrodolomite (Figure 4.4). The carbonate minerals are interpreted to have been formed as primary precipitates and from early diagenetic dolomitization (Pitman, 1996). Thus, the framework and sheet silicates of R0 are interpreted to be the primary minerals from which all other authigenic and diagenetic phases in the GRF formed, with additional contributions from high quantities of organic matter (Surdam and Parker, 1972; Smith, 1983).

5.2 Stratification of Lake Waters and Transition Zones

Density differences between cold and warm waters are the main cause of initial stratification in continental lacustrine basins. Exposure to wind keeps the upper layer of water well-circulated and oxygenated, and it is warmed by solar radiation (Drever, 1997). By contrast, deeper waters which are colder and denser experience little wave action or vertical exchange with warmer, low-density upper waters. Stratification may become permanent especially in deeper lakes in warmer climates, which do not experience seasonal overturn as result of annual cooling of the upper layer of water (Demaison, 1980; Drever, 1997; Last and Ginn, 2005). Therefore, exchange of solutes between the two layers of water may be very limited, and persistent chemical stratification may also develop, with a lower water mass of higher salinity, and a more dilute upper water mass (Drever, 1997).

These three main factors were most likely also responsible for permanent stratification of the water column in paleolake Uinta: temperature, density and chemistry (Demaison, 1980; Smith, 1983; Drever, 1997). Initially, colder, denser waters sank to the bottom of the lake, and low energy levels in the deeper basin allowed for very little replenishment of oxygen from lack of mixing with upper, warmer waters (Demaison, 1980; Last and Ginn, 2005). The initial stratification assisted in establishing and maintaining anoxia in the stagnant bottom waters of the lake, where the decay of organic matter allowed for a reducing environment to evolve relatively quickly (Demaison, 1980; Smith, 1983). Nutrient-rich fluvial run-off mixed with surface waters
at the basin margins, sustaining an oxic and fresher upper layer, where highly productive photosynthetic organisms served as the source of abundant organic matter (Desborough, 1978; Démaison, 1980; Eugster, 1985). The formation of a chemical gradient also came about as a warming climate was coupled with decreased precipitation and less freshwater fluvial input into the basin (Tänavsuu-Milkeviciene and Sarg, 2012). Evaporative concentration increased the precipitation of minerals that deposited in the sediments in contact with the lower water layer. As calcium and magnesium precipitated and were depleted from the water column, buffering by the carbonate system would be exhausted, allowing the pH to rise to 10 or higher. As the resulting alkaline conditions degraded detrital minerals at the sediment-water interface of the basin center, concentrations of dissolved salts increased in the lower water layer. This raised the density and salinity contrast of the two layers of water, creating a chemocline at the boundary between them (Desborough, 1978; Eugster, 1980; Smith, 1983; Drever, 1997).

The composition of pore waters is originally sourced from the overlying water column above the sediments being buried, and subsequently from dissolution of minerals in contact with pore waters during early diagenesis (Boggs, 1992, Krauskopf and Bird, 1995, Pitman, 1996). Therefore pore water composition correlates to the location in the basin and to the depth of the chemocline during that stage in Lake Uinta’s history. Trapped pore waters near the basin margins would be more likely to derive from the shallower upper water layer above the chemocline, which would be generally fresher (Last and Ginn, 2005; Tänavsuu-Milkeviciene and Sarg, 2012). In contrast, pore waters from locations closer to the basin center would be more likely to derive from the deeper, denser water layer below the chemocline, and consequently be more alkaline, reducing, and saline. Consequently, the formation of authigenic minerals in pore waters after burial are imprinted with the water chemistry of the location and time in the basin where their precursors were deposited. Secondary minerals that formed during early diagenesis are thus indicative of the boundaries and chemical conditions of the lower layer of water at the time of sedimentation, just as authigenic minerals that precipitated directly from the water column of the lake are, such as calcite, halite and bedded nahcolite.

The chemocline defined the boundaries of the contrasting conditions of the water column in contact with sediments in the basin margin versus the basin center. The contrast in mineral assemblages between the basin center sections and basin margin outcrops attest to the simultaneous coexistence of very different environments of deposition in shallower vs. deeper
waters of the basin. Mineral assemblages exhibit less stratigraphic variation in the basin margin samples than in basin center samples, suggesting that nearshore water conditions in the upper water column layer were relatively more stable for the duration of the paleolake history. The relatively constant occurrences of carbonate minerals, clay minerals, and analcime throughout the vertical section of the basin margin, and lack of discernible transition zones, suggests that changes in the water chemistry of the upper layer of water in contact with margin sediments were less extreme and more ephemeral than that of the lower layer of water in contact with sediments of the basin center. By contrast, the mineral assemblages of the basin center records major changes in the lake chemistry of the lower water layer to extreme conditions which endured for millions of years below the chemocline (Dyni, 1998). Therefore, the distribution of authigenic minerals in the GRF may be interpreted as a gauge of the extent and depth of the chemocline separating the stratified upper and lower water layers during each lake stage (Figure 5.1).

**Figure 5.1** Cartoon of stratification in Lake Uinta, illustrating the separation of the upper and lower layers of water by the chemocline (yellow dashed line). The chemocline fluctuated in depth and therefore lateral extent (arrows). Green River Formation sediments of the basin margin were in contact with the upper, fresher layer of water, and sediments of the basin center were in contact with the lower, stagnant layer of water. Pore waters under the basin center water column therefore were more reducing, had higher alkalinity and higher salinity, whereas the pore waters under the basin margin water column had less extreme chemical properties. This separation allowed for the formation of different authigenic mineral suites in the basin margin and in the basin center.

Smith (1983) interprets the sudden change in mineralogy at the lower transition zone of the stratigraphic column as a point when a critical pH was reached (Smith, 1983). This thesis proposes that the lower transition zone may be indicative of the timing at which stable stratification was first established at that location in the basin center, and/or the sediments were
first submerged below the level of the chemocline. This theory assumes that the chemocline fluctuated in depth and therefore lateral extent over time, in response to tectonic and climate influences (Dyni, 1998; Last and Ginn, 2005; Tänavsuu-Milkeviciene and Sarg, 2012). Likewise, the upper transition zone may be indicative of the point in time at which stratification weakened, and/or when the chemocline retreated from that location in the basin, as it shrank to cover a smaller area of the basin center. The extent and depth of the chemocline would have experienced migration as tectonic and depositional trends tied to climatic influences changed the morphology of the basin (Feng, 2011; Tänavsuu-Milkeviciene and Sarg, 2012). The depocenter of the Piceance Basin has been shown to have moved and changed shape over the history of the lake, by isopach maps of lake Stages 2 through 5 by Feng (2011) (Figure 5.2). Steep basin slopes are indicated by rapid changes in thickness from basin margin to basin center in lake Stages 2 and 3, which would have deepened the lower layer of saline water, and caused the aerial extent of the chemocline to be restricted (Feng, 2011). As gradients in the lake basin became more gradual in Stages 4 and 5 as shown in figure 5.2, a theoretical equal volume of the lower layer of saline water would spread out and become thinner, causing the chemocline to expand and cover a larger area of sediment (Feng, 2011).

Tänavsuu-Milkeviciene and Sarg, 2012, have interpreted Stage 4 to have experienced greater precipitation as a consequence of a cooling, more humid climate. Yet, Lake Uinta remained stratified through Stage 6 despite the corresponding increase in freshwater inflow, increased frequency of siliciclastic turbidite deposits, and rising lake levels (Tänavsuu-Milkeviciene and Sarg, 2012). The increased freshwater contributions would have served to swell the volume of the upper, fresher water layer. In response, the chemocline may have retreated to lower depths, as the lower, more saline layer of water decreased in volume, or alternatively, stratification may have weakened from a decrease in the concentrations of the lower water layer, so that the density and salinity contrast between the two layers was lessened.

During the more arid periods of greater evaporative concentration and lesser precipitation in the lake’s history (lake Stages 2 and 3 in the middle MU), the upper, fresher water layer would have become thinner from evaporative loss and decreased freshwater replenishment (Tänavsuu-Milkeviciene and Sarg, 2012). The lower, more saline water layer would be likely to have encompassed a greater proportion of the volume of the lake. With increasing solute concentrations, greater volumes of water would experience increased density, which may have
Figure 5.2 Contours representing the depositional extents of saline minerals nahcolite and halite, from Dyni (1996), overlayed on isopach maps of lake stages 2 through 5, contour interval 20 ft (from Feng, 2011). The thickest areas of deposition trend from NW to SE and show migration of the depocenter during lake history. Deposition during the most saline periods of the lake in Stages 2 and 3 is shown to have occurred in a deep basin with steep sloping sides. Basin morphology changed to lower slope gradients in Stages 4 and 5. Modified from Dyni, 1996, Feng, 2011, and Tänavsuu-Milkeviciene, 2012.

caused the chemocline to rise and expand as the more saline portion of the water column would thicken. Consequently, a greater area of the bottom sediments in the basin center would be covered by the more saline bottom water layer. Likewise, the area of sediments in contact with
the upper fresher layer of water would become a thinner rim around the basin margin. It is therefore postulated that the transition zones are less well defined in sediments further from the basin center, which experienced shorter periods of time below the chemocline, and possibly multiple periods of “submersion” of bottom sediments midway between the basin center and basin margins. This would also explain the indications of brief nahcolite deposition in small quantities in the basin margin samples in this thesis, the presence of oil shale facies in basin margin sections, and other saline minerals reported detected in sections closer to the basin margin in other published studies (Brobst and Tucker, 1973; Cole and Picard, 1978). Therefore, transition zones are not chronostratigraphic boundaries, except where sediments nearest to the basin center remained submerged below the chemocline for the duration of the existence of the stable stratification of the lake. Comparisons of figures 4.5, 4.6, 4.7, and 4.8 show that there are slight difference in the stratigraphic position of the upper and lower transition zones between the sections of CR-2, CO-1, the John Savage 24-1 and Shell 23X-2, as each core occupies different positions in the basin relative to the basin center. Brobst and Tucker (1973) also note that time-stratigraphic units are cross-cut by dawsonite deposition. Evaluations of sections which are further from the basin center than the four cores used in this thesis would serve to clarify this alleged nature of the transition zones and associated dynamic history of the chemocline in Lake Uinta.

5.3 Mineral Units

The lower mineral unit (MU) assemblages are interpreted to consist of mainly detrital phases and the products of weathering reactions as would deposit in a more typical sedimentary environment of a fresh water lake. Mineral assemblages are the most similar between the basin margin and the basin center sections in the lower MU and represent a relatively fresh to brackish environment in both basin locations (Figures 4.1, 4.2, Table 4.3) (Surdam and Parker, 1972). Although, even during the earliest portion of the lower MU the basin center waters were already more brackish than in the basin margin, as evidenced by V/Cr ratios, an almost continual occurrence of relatively low quantities of buddingtonite, and higher proportions of ferrodolomite in the basin center (Figure 4.23) (Dyni, 1997; Eugster, 1980). In the lower MU of both the Douglas Pass and Shell 23X-2, quartz occurs in quantities of over twice that of total feldspar (Figure 4.34), with relatively lower buddingtonite, abundant clay minerals (of diverse types in
the basin margin), relatively more abundant calcite and aragonite, relatively low organic matter quantities, and a lack of saline minerals (Figures 4.3 and 4.4). A similar fresh to brackish mineral assemblage continues throughout most of the basin margin stratigraphic section in the middle and upper MUs, and points to shallower margin sediments being in almost continual contact with a relatively less saline upper layer of water throughout the lake history (Figure 5.1).

In the middle MU, mineral assemblages greatly diverge between the basin center and the basin margin as stratification became established, and authigenic minerals began to comprise a much larger part of the assemblage. The main change in the basin margin assemblage is in the addition of the authigenic mineral analcime, and greater proportions of feldspar, both of which are indicative of slightly higher alkalinity (Eugster, 1980). In the basin center, the change in assemblages is much more significant, with the addition of high quantities of saline minerals and large shifts in proportions of the types of silicate and carbonate minerals. The middle MU of the basin center is almost devoid of clay minerals, and the ratio of quartz to total feldspars decreases to less than one in most of the section. Minerals of the middle MU tell of a significant increase in both alkalinity and salinity in both basin locations, but to a much higher degree in the basin center (Figure 5.3) (Surdam and Parker, 1972). The contrast in the middle MU of the two basin locations supports the existence of a permanently stratified water column in Lake Uinta, with more extreme geochemical conditions in the lower water layer below the chemocline than in the upper layer of water (Table 4.3).

In the upper MU, mineral assemblages converge again to a certain extent between the two basin locations. Assemblages in the basin center begin to resemble that of the less saline set in the lower MU, with a few exceptions, such as the continuation of nodular nahcolite. Most significantly, analcime and calcite return, indicating lowered alkalinity and higher silica activity; and quantities of saline minerals are greatly reduced, no longer occurring in bedded form, which may be indicative of less persistant stratification and much reduced salinity. Pore waters likely remained more alkaline and saline than the overlying water column as saline minerals continued to deposit in nodular form. Buddingtonite occurs in much lower quantities indicating that reducing conditions lessened, and interactions between organic matter and minerals may have been reduced (Demaison, 1980; Eugster, 1980; Smith, 1983).
5.4 Geochemical Conditions of Paleolake Waters

Three main factors in water chemistry evolved in the water column and sediment pore waters of paleolake Uinta, beginning with reducing conditions, increasing pH, and finally hypersalinity, which combined to degrade detrital minerals and create multiple new phases (Surdam and Parker, 1972; Cole and Picard, 1978; Eugster, 1980; Smith, 1983; Smith et al., 1987; Stamatakis, M.G., 1989; Bristow, 2012). Reducing conditions developed very early in the lake history and appear to have behaved independently of pH and salinity, according to mineral assemblages and redox proxy indicators. The most anoxic conditions occurred in the lower MU of both the basin center and basin margin, and then decreased to more moderate dysoxic levels in the middle and upper MUs, without much of a change at the upper transition zone. In contrast, saline and authigenic aluminosilicate mineral assemblages indicate that pH and salinity were more interrelated and both significantly rose in the middle MU of the basin center (Figure 5.3).

Figure 5.3 Idealized cartoon of general changes in water chemistry under the chemocline of the basin center in the lower, middle, and upper mineral units. Fluctuations in alkalinity and salinity roughly parallel each other, both increase or reach a critical value near the lower transition, and begin to subside at the upper transition zone, whereas reducing conditions increase early in the lower mineral unit and decrease to moderate values at the lower transition.
Authigenic sodium-aluminum-bearing minerals greatly increased in quantities at the lower transition zone, suggesting that a critical alkalinity was reached at the end of the lower MU. Shortly afterward, saline minerals began to deposit in elevated quantities in the middle MU, a little later than alkaline minerals. Saline mineral deposition continued into the upper MU, albeit in reduced amounts, depositing longer than minerals indicative of elevated alkalinities, which began to subside at the upper transition zone (Figures 4.23 and 5.3).

5.4.1 Organic Matter and Biotic Contributions

Organic matter content in oil shale typically ranges from 10 to 65 dry weight % (Mõtlep et al., 2007). The GRF in the PCB is the most organically rich of all the basins where the GRF deposited. TOC analysis by SRA pyrolysis by Feng, 2011, uses a larger sample set than analyzed by this thesis by XRD, and has greater correlation to other measures of organic richness including Corg by IR (Feng, 2011) (Supplemental File L). According to the SRA data, TOC is as high as 45 % in the basin center, with an average of 17%. In the basin margin, TOC ranges from 0.2 to 26 %, with an average of 4 % by SRA (Feng, 2011). The highest quantities of organic matter are found in the middle MU of the basin center, reflecting a combined set of conditions favorable to both the deposition and preservation of organic matter (Feng, 2011). Productivity is interpreted to have been high with minimal dilution by clastic minerals in the middle MU. Although saline mineral deposition was high below the chemocline in the middle MU of the basin center, generation of organic material from the upper layer of water was greater (Feng, 2011).

The deposition of high quantities of organic matter and the formation of authigenic and diagenetic minerals are intrinsically linked in the GRF. When high proportions of organic material accumulate in the siliciclastic sediments, bacterial degradation has a great effect on the chemistry of the pore waters and water column. (Boggs, 1992). Oxidation of organic matter consumes oxygen from the water column, which increases reducing conditions in the bottom of the lake (Demaison, 1980; Smith, 1983). Carbon dioxide produced from the breakdown (decarboxylation) of organic matter, becomes bicarbonate and carbonate ions, raising the alkalinity of the waters (Krauskopf and Bird, 1995; Smith, 1983). Resulting high pH conditions subsequently reduce the stability of aluminosilicate minerals, increasing the activity of other elements such as silica and alumina (Surdam and Parker, 1972). Therefore, the presence of large
quantities of degrading organic matter served to facilitate reactions between detrital minerals and soluble ions in the water, which ultimately led to the formation of authigenic and diagenetic minerals (Smith, 1983).

High concentrations of organic matter in the GRF of the PCB are a reflection of high preservation rates under an anoxic water column, but also indicate that productivity must have remained high in order to generate such high quantities (Smith, 1983; Boggs, 1992). This necessitates the existence of an upper less saline zone of lake water where organisms could thrive, even during the most saline periods in the paleolake’s history (Demaison, 1980; Smith, 1983; Feng, 2011). In fact, concentrations of organic matter are greatest the middle MU of the basin center, where saline minerals are the most abundant (Table 4.3). Therefore, abundant quantities of organic matter in the GRF serve as evidence to support the theory that waters were stratified into a fresher upper layer and more saline lower layer in most lake stages (Cole and Picard, 1978; Desborough, 1978). See Supplemental File L for organic matter results.

Photosynthetic cyanobacteria are thought to have been the dominant organisms in Lake Uinta, and main source of organic matter in the PCB, because they can survive in waters with elevated salinities and alkalinites where other organisms cannot (Desborough, 1978). Cyanobacteria are capable of fixing nitrogen, and the organic matter of the GRF is documented as being high in nitrogen (Baughman, 1978). Organic matter is likely to be the source of ammonia for buddingtonite. Therefore, high organic matter content in the sediments served as the source of carbon, as well as nitrogen for reactions producing authigenic minerals.

The production of carbonate from the degradation of organic matter can convert sulfate ions to hydrogen sulfide (Equation 5.1). The absence of sulfate minerals is a notable aspect of the mineralogy of the GRF (Dyni, 1996, 2006). The latter process effectively removes sulfur from the system either by venting the gas or by later reduction to form sulfides ((Desborough, 1978; Krauskopf and Bird, 1995):

\[
\text{Organic matter + sulfate } \rightarrow \text{ bicarbonate + hydrogen sulfide}
\]

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}
\]

(5.1)

Authigenic sulfate minerals are only found in trace amounts in the PCB, even though sulfate was most likely abundant in the rivers and run-off water that fed lake Uinta. This may be explained by sulfate reduction by bacteria in the anoxic, stratified waters, and reaction with iron in the sediments to form pyrite (Dyni, 2006; Dyni, 1996). GRF sediments are also unusually rich
in iron-bearing carbonate minerals Desborough (1978). The high ferrous iron content of diagenetic carbonate minerals is likely related to the lack of sulfate minerals found in the GRF. As a result of sulfate-reducing bacteria activity in anoxic pore waters, sulfur concentrations may have been nearly completely depleted, and lost from the basin as gas. Therefore, pyrite formation did not exhaust ferrous iron during diagenesis, making it available for the formation of ferrodolomite (Desborough, 1978; Krauskopf and Bird, 1995; Pitman, 1996).

Biotic processes likely had a great influence on orthochemically precipitated carbonate mineral deposition in the GRF, as well as on the chemical stratification of the lake waters (Desborough, 1978; Pitman, 1996). Photosynthetic organisms in the upper near-surface waters consumed CO$_2$ and produced oxygen, contributing to the contrast with the anoxic to dysoxic and alkaline conditions below the chemocline in the lower near-sediment waters (Demaison, 1980; Desborough, 1978). Resulting decreased concentrations of CO$_2$ in the upper water layer caused calcite precipitation, lower dissolved carbonate ion concentrations, and increasing Mg$^{2+}$/Ca$^{2+}$ ratios (Eugster, 1980). In contrast, in the lower water layer, abundant CO$_2$ was likely generated at the sediment-water interface by degradation of organic matter (Pitman, 1996). Degradation of algal bodies which settled to the bottom also served as a source of iron, magnesium, calcium, potassium, sodium, phosphorous and sulfur for reactions to produce authigenic mineral phases in the pore waters of bottom sediments (Desborough, 1978). High magnesium concentrations present in chlorophyll would have been readily released from organic matter by the highly alkaline conditions of the lower layer of water, increasing the rate of dolomitization in sediments below the chemocline (Desborough, 1978).

5.4.2 Redox Conditions

Redox conditions in nonmarine environments of deposition are normally oxic to slightly anoxic initially (Boggs, 1992). The depletion of dissolved oxygen by the process of eutrophication is a common phenomenon in fresh bodies of water that are rich in organic and mineral nutrients (Demaison, 1980; Drever, 1997). Large lakes in warm climates, which support abundant plant life, especially algae, are prone to the development of anoxia due to a higher demand for oxygen than is available in deeper waters (Demaison, 1980; Drever, 1997). Dysoxia is indicated by the redox proxy V/Cr ratios to have developed early at the base of the lower MU, in both the basin margin and basin center (Figures 4.22, 4.23). The fact that
buddingtonite, an ammonium feldspar, is present in the deepest R0 sample of the basin center, supports the theory that conditions became reducing very early in the lake’s history (Figures 4.1, 4.4) (Smith, 1983). As ammonium is the most reduced form of nitrogen, low redox potential is necessary to convert nitrogen species to NH$_4^+$ before buddingtonite may form. The qualitative parallel relationship found between redox indicators and buddingtonite in this thesis suggests that reducing conditions are one control on its formation (Figure 4.25). High alkalinity is also a requirement to destabilize precursor aluminosilicate minerals, as well as the presence of a high quantity of organic matter to provide a source of nitrogen (Surdam and Parker, 1972; Baughman, 1978). Buddingtonite is likely to have formed as a solid solution with alkali feldspars by substitution of NH$_4$ for potassium, but its occurrences suggest that buddingtonite does not form according to the same set of conditions as the other feldspars (Krohn et al. 1993; Oh et al. 1993). Both Na-K-Ca feldspars and buddingtonite quantities increase in the middle MU at the lower transition zone, but at the upper transition zone Na-K-Ca feldspar quantities remain high or increase, whereas buddingtonite quantities greatly decrease (Figures 4.7 and 4.8). In addition, the highest quantities of buddingtonite and the highest quantities of Na-K-Ca feldspars do not occur in the same set of rock type samples (Table 4.6). Siltstone is the richest of all rock types in Na-K-Ca feldspars in the basin center, and sandstone is the richest rock type in Na-K-Ca feldspars in the basin margin. Notably, no sandstone samples contain any buddingtonite, despite the fact that they are very arkosic. In contrast, buddingtonite occurs at the highest quantities in mudstone samples, and marlstone samples contain the second highest buddingtonite quantities, in both basin locations (Supplemental File N). Therefore, the set of required conditions are not the same for the formation of buddingtonite as for other feldspars, and reducing conditions are suggested to be a distinct control for buddingtonite, which does not apply to Na-K-Ca feldspars.

Dysoxic conditions allow for the formation of high-iron forms of carbonate minerals, which commonly become the dominant carbonate species in highly reducing aqueous geochemical environments (Deer et al, 1992; Krauskopf and Bird, 1995). The reduction of ferric iron (Fe$^{3+}$) to ferrous iron (Fe$^{2+}$) makes iron more available for reaction as ferrous is more soluble than ferric iron (Desborough, 1978; Smith, 1983; Krauskopf and Bird, 1995). The formation of Fe-rich dolomite requires reduced iron to be available, as ferrous iron (Fe$^{2+}$) is required for substitution of Mg$^{2+}$ (Smith, 1983; Krauskopf and Bird, 1995). Reduction of ferric iron oxides as a result of bacterial degradation also releases hydroxyl ions which increases the
pH. This contributes to the alkalinity in pore waters of shallow sediments, where many authigenic minerals form, and dolomitization occurs (Boggs, 1992). Ferrodolomite is present in large quantities in samples from rich zone R0, in the lower MU of the basin center section. This furthers the argument that reducing conditions were established in the initial stages of GRF deposition, long before the lake became highly saline. Ferrodolomite also increases at the lower transition zone, when redox conditions decrease according to redox proxies and where alkalinity is proposed to have increased (Figure 4.1). Therefore alkaline conditions in pore waters during early burial is proposed as another required condition of high-iron dolomitization.

The qualitative correlation that is evident between the geochemical redox proxy V/Cr and ferrodolomite quantities in this thesis suggests that reducing conditions were a control on the formation of iron-rich dolomite in the PCB (Figure 4.24). V/Cr values parallel ferrodolomite quantities in the basin center John Savage 24-1 section, and Douglas Pass basin margin section, but a relationship is less apparent in the lower basin center Shell 23X-2 section. The qualitative correlation is strongest for ferrodolomite in the margin section, where fresher conditions were more likely to have prevailed (Figure 4.24). The correlation between ferrodolomite and the redox proxy is also most evident in the lower and upper MUs of the Douglas Pass basin margin section, therefore reducing conditions may have been a stronger control on dolomitization in sequences that deposited during the less saline intervals of lake history, whereas alkalinity and the (Mg+Fe)/Ca ratio may have acted as stronger influences on ferrodolomite deposition in deeper basin locations, and during more saline stages of the lake.

5.4.3 Na-Al Minerals

The formation of authigenic and diagenetic aluminosilicates is largely dependent on the pH of the water column and pore waters of sediments. In general, silica activity increases with alkalinity, and concentrations of SiO$_2$ in solution are much greater once the pH surpasses 9.0, making silicon more available for reaction with other ions (Surdam and Parker, 1972). The solubility of alumina is lower than that of silica at pH 8.0, but it becomes just as mobile when alkalinity increases to over pH 10.0 (Surdam and Parker, 1972; Smith, 1983). Smith (1983) interprets the pH of the water column in the GRF of the PCB to have been over ten at times, and up to an average of 11 in lake stages associated with the highest organic matter concentrations. As degradation of organic matter generates CO$_2$, the pH rises as it goes into solution, producing
carbonate and bicarbonate. Therefore, a relationship between organic matter concentrations and quantities of authigenic silicates would be predicted (Smith, 1983). Robb and Smith (1974) identified a positive relationship in the CO-1 core between organic matter and the silicate minerals quartz, albite and potassium feldspar, but none was recognized in this study. Alkalinity is also attributed in the literature to detrital contributions from volcanic ash to the lake waters (Surdam and Parker, 1972; Brobst and Tucker, 1973; Dyni, 1998). Buffering by carbonates in the sediments likely kept the pH between 8.5 and 10 in interstitial pore waters (Surdam and Parker, 1972; Smith, 1983). Therefore, the pH may have abruptly decreased at the sediment-water interface, which may have caused authigenic feldspars and other aluminosilicates to crystallize as the solubility of silica and alumina decreased accordingly (Smith, 1983).

Elevated alkalinity of paleolake waters is likely to be one cause of the high proportions of feldspars throughout the GRF of the PCB, and the low quartz to feldspar ratios exhibited in both basin locations (Figure 4.34). Higher proportions of albite in the basin center feldspar assemblage than in the basin margin are an indication that a large part of feldspars in the basin center are likely of authigenic origins. The ratio of sodic to potassic feldspars in the basin center is 0.80, which is a significant increase over the basin margin ratio of 0.56. This is reflective of much greater sodium concentrations in the basin center, as well as elevated alkalinity. As pH rose, detrital aluminosilicates were altered, making Si and Al available in the sediments for the formation of authigenic minerals such as feldspars, and Na concentrations to rise in the water column (Eugster, 1980; Surdam and Parker, 1972).

The clay-rich lower MU of the stratigraphic section in the GRF (Garden Gulch member) is a consequence of the preservation of the alteration products of weathering reactions during a time when conditions in the lake were fresh to brackish (Eugster, 1980; Smith, 1983). High quantities of clay minerals, other sheet silicates, and authigenic quartz in the lower MU were deposited from the hydrolysis of detrital arkosic sediments early in the lake history, suggesting that conditions of intense weathering existed in that period. As water conditions became increasingly basic in successive paleolake stages (the Parachute Creek Member), clay minerals became unstable and subsequently degraded. Weathering reactions were then driven in the opposite direction, to consume sheet silicates and create authigenic feldspars in the deeper part of Lake Uinta below the chemocline, especially in the middle MU, (Surdam and Parker, 1972; Eugster, 1980; Smith, 1983; Boak and Poole, 2014). Reversible reactions between feldspar
minerals and clay minerals are illustrated by the following example equations (Equation 5.2), which uses illite to represent a clay mineral end member, and albite as the representative feldspar end member (Eugster, 1980; Krauskopf and Bird, 1995; Boak and Poole, 2014).

\[
\text{Albite} \leftrightarrow \text{Illite} + \text{Quartz} \\
3\text{NaAlSi}_3\text{O}_8 + \text{K}^+ + 2\text{H}^+ \leftrightarrow \text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + 6\text{SiO}_2 + 3\text{Na}^+ \tag{5.2}
\]

The transition from a clay mineral-rich assemblage with quartz and only minor feldspar quantities in the lower MU, to an assemblage rich in feldspar and quartz, with only minor clay minerals in the middle MU, strongly supports the conclusion that the above reaction was driven to the left in the basin center. Limited exclusive relationships were identified in this thesis between quantities of feldspar and illite/smectite clay minerals in the basin center, and may represent an illustration of the equilibrium between reactant and product minerals in similar reverse weathering reactions (Figure 4.32). A similar limited exclusive relationship is also illustrated in figure 4.32 in the basin margin section between kaolinite and potassium feldspar (Eugster, 1980).

Surdam and Parker (1972) observed that authigenic clay minerals and zeolites are found in fresher water facies, whereas authigenic feldspars formed in hypersaline facies of the GRF in Wyoming (Surdam and Parker, 1972). Smectite only occurs at less than 10% in samples that contain authigenic aluminosilicates, and is absent when analcime or feldspar is present (Surdam and Parker, 1972). It is suggested by Surdam and Parker (1972) that smectite alters to illite in the same set of chemical conditions that analcime deposits. At lower pH, clay minerals would be the preferred mineral phase, and at slightly higher pH zeolites are the initial authigenic phase (Surdam and Parker, 1972). As pH increases, smectitic clay minerals begin to form instead of kaolinite, and finally illite is formed in place of smectite (Smith, 1983) (Figure 4.10). Minor clay minerals, including kaolinite, in this thesis are found almost exclusively in the basin margin section, where fresher conditions than those found in the basin center existed throughout the basin history. The smectitic composition of the basin margin samples in this study are therefore indicative of conditions within a relatively low range of alkalinity, and the presence of analcime is indicative of a slightly higher range of alkalinity (Figure 4.19). In the basin center, a higher range of elevated alkalinity is suggested due to the predominance of illite in the lower and upper MUs.
Zeolites are authigenic silicates often associated with alkaline, evaporative, sedimentary formations and postulated to form from the alteration of volcanic glass (Surdam and Eugster, 1976; Eugster, 1980 p. 39). Most commonly, analcime forms from other precursor zeolites in saline alkaline lake settings, but in the GRF of the PCB, there is no XRD evidence of any other zeolite minerals (Surdam and Parker, 1972; Surdam and Eugster, 1976). Alkalic zeolite minerals may be synthesized in the laboratory in alkaline solutions of pH 9.0 to 10.5 from aluminosilicate gels and glass with high silica contents (Surdam and Parker, 1972; Deer et al. 1992). Therefore, analcime is likely to be an indicator of moderately elevated pH in the pore waters of the sediments of the GRF, and deposits as a lower-silica authigenic aluminosilicate when Si/Al ratios are low (Figure 4.37) (Surdam and Parker, 1972; Surdam and Eugster, 1976). Analcime may react to form higher-silica-content authigenic feldspars as alkalinity continues to increase and concentrations of mobile silicon, aluminum and potassium increase (Surdam and Parker, 1972). Thin section analysis of samples from the GRF in the Wyoming Basins showed that analcime can be replaced by potassium feldspar (equation 5.3) (Surdam and Parker, 1972; Surdam and Eugster, 1976; Deer et al. 1992).

\[
\text{Analcime} + \text{Quartz} \leftrightarrow \text{K-Feldspar}
\]

\[
\text{NaAlSi}_2\text{O}_6*\text{H}_2\text{O} + \text{SiO}_2 + \text{K}^+ \leftrightarrow \text{KAlSi}_3\text{O}_8 + \text{H}_2\text{O} + \text{Na}^+
\]

Analcime has also been decomposed into albite in the presence of quartz (Deer et al. 1992). This provides an explanation for the deficiency of analcime in the basin center, and its disappearance in the middle MU, where more extreme conditions may have degraded analcime and deposited other authigenic aluminosilicate phases in its place. The pH values of zeolite formation in the laboratory setting may provide for a tentative assignment of quantitative values to the alkalinity for which analcime degraded and related authigenic phases formed in the environments of deposition of Lake Uinta.

Brobst and Tucker (1973) observed that analcime inversely varied with dawsonite quantities, which was not confirmed in this thesis, however a limited co-occurrence was recognized between dawsonite and analcime at less than 5 wt% (Figure 4.28). Brobst and Tucker (1973) also found that dawsonite quantities directly vary with quartz, which was confirmed by this thesis as a positive, quantitative relationship (Figure 4.26). The high coefficient of determination, \(R^2 = 0.85\), between dawsonite and quartz values may be a consequence of both minerals being equally proportioned products in the same reaction in which the parent minerals
are being altered. These relationships led Brobst and Tucker to suggest that dawsonite is an alteration product of analcime when concentrations of CO\textsubscript{2} are high (equation 5.4) (Brobst and Tucker, 1973).

\[
\text{Analcime} + \text{Carbon Dioxide} \rightarrow \text{Quartz} + \text{Dawsonite}
\]

\[
\text{NaAlSi}_2\text{O}_6 * \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{SiO}_2 + \text{NaAlCO}_3(\text{OH})_2
\] (5.4)

The presence of hydroxide in the chemical formula of dawsonite attests to a tie between its formation and higher pH values. Laboratory studies have shown that dawsonite can be synthesized from a sodium aluminate solution as CO\textsubscript{2} is bubbled through and alkalinity is brought down from an initial pH of 11 (Smith, 1983). Equation 5.4 would support the idea that analcime is stable at a lower range of alkalinity than dawsonite (Smith, 1983; Krauskopf and Bird, 1995). Brobst and Tucker (1973) found that analcime compositions had higher Si/Al ratios in samples with dawsonite than analcime in samples that contained no dawsonite, and attributed it to analcime providing the aluminum and silicon needed for dawsonite and quartz formation. In this thesis, the limited exclusive relationship between the two minerals in samples from the two end-member basin locations, suggests that all analcime was altered to dawsonite in the middle MU of the basin center, where sediments experienced the most sustained high pH conditions, and very little if any analcime was altered to dawsonite in the basin margin where waters are thought to have remained at low to moderate pH.

If dawsonite formation requires a different range of conditions relative to analcime, then it may be inferred that since analcime and calcite have similar occurrences, that dawsonite and calcite also have separate conditions of formation, and a limited exclusive relationship should theoretically exist between them. Figure 4.30 confirms this hypothesis and demonstrates that calcite and dawsonite do not co-occur in the same samples above 6 wt%, similar to the limited exclusive relationship identified between dawsonite and analcime (Figure 4.28). Overlap in occurrence of the two minerals might be attributable to calcite being emplaced as secondary cement during later diagenesis, after dawsonite crystallized in pore waters.

Brobst and Tucker (1973) and Surdam and Parker (1972), among others, point to the importance of reactions among minerals with constant Na:Al ratios but differing Si content as guiding which authigenic phase is formed in the Green River Formation. Dawsonite competes with aluminosilicates for aluminum and sodium (Hellavang et al. 2011). The relative stabilities
of dawsonite, feldspar, and clay minerals are determined by a combination of pH, temperature, and the activities of dissolved silica, sodium and carbonate (Surdam and Parker, 1972; Smith, 1983; Hellavang et al. 2011). An activation barrier controlled by temperature must be overcome before formation of dawsonite may begin according to Hellavang et al. (2011). Temperatures in the deep, saline aquifer of Lake Uinta may have been elevated due to the degradation of large quantities of organic matter, reducing the energy barrier to dawsonite (Hellavang et al. 2011). In general, according to phase diagrams by Hellavang et al. (2011), dawsonite forms at lower silica activities than albite, and at higher sodium activities relative to hydrogen activity (pH) than kaolinite (Figure 5.4). Since only trace quantities of kaolinite were identified in the basin center, it may be assumed that high sodium concentrations and/or high pH operated in the pore waters of the basin center for the majority of the duration of Lake Uinta. The separate conditions of formation for analcime and dawsonite inferred by relationships identified in this thesis are likely to be consequences of the same factors that control the stability fields of dawsonite vs. feldspar (Surdam and Parker, 1972; Smith, 1983; Hellavang et al. 2011). Sodium activities are shown to be an important control on analcime formation by the positive relationship identified between analcime and Na$_2$O quantities in this thesis in the basin margin (Figure 4.35). Silica activities are also important as demonstrated by the negative relationship between analcime and Si/Al identified in this thesis in the basin margin (Figure 4.37). The relationship between low silica activity and analcime may be extended to the basin center to theorize that dawsonite forms when silica activity decreases further, in place of analcime and instead of higher Si-content feldspars. No relationship between dawsonite and concentrations of SiO$_2$ or Si/Al could be found in the datasets of this thesis, except for the quantitative positive linear relationship identified between quartz and dawsonite in the middle MU of the basin center (Figure 4.26). Likewise, Na$_2$O concentrations positively correlate with nahcolite, but not with dawsonite or plagioclase in the basin center of the GRF, as figure 4.36 indicates.

Brobst and Tucker (1973) suggested that dawsonite may have precipitated directly from waters due to the availability of aluminum from aluminosilicates which degraded at elevated alkalinites. The lack of bedded dawsonite, and disseminated dawsonite crystals identified in thin sections, suggest that if this were a possibility, precipitation did not occur in the water column, but in pore waters. Dawsonite, analcime, and authigenic feldspars most likely crystallized in pore waters at or below the sediment-water interface, where relatively insoluble alumina would be
Figure 5.4 Phase diagram of stability fields for dawsonite, albite, kaolinite and quartz, including SiO$_2$ activity range for quartz, and saturation limit for nahcolite. The fact that kaolinite is not found above trace concentrations in the basin center, suggests that conditions below the chemocline were maintained at high Na$^+$ activities and/or low H$^+$ activities. From Hellavang et al. 2011.

most available (Surdam and Parker, 1972; Smith, 1983; Krauskopf and Bird, 1995; Boak and Poole, 2014; Jagniecki and Lowenstein, 2014). It has also been suggested that critical alumina activity may define a minimum pH required for the initiation of dawsonite formation, although Hellavang et al. (2011) suggests that this is probably a very low pH, and therefore not a limiting factor in alkaline lake waters (Smith and Milton, 1966; Smith, 1983; Eugster, 1980; Krauskopf and Bird, 1995; Hellavang et al. 2011). Clay minerals may serve as the primary source of aluminum for the formation of authigenic Al-bearing minerals. The near-absence of clay
minerals in the middle MU suggest that they are unstable in the conditions that dawsonite forms. This may also be inferred by the appearance of dawsonite in the stratigraphic column of the basin center just as feldspars greatly increase, and as clay minerals significantly decrease at the lower transition zone. The link between the breakdown of clay minerals and the formation of authigenic Al-bearing minerals is also supported by limited exclusive relationships between dawsonite and total clay minerals; and between the sum of dawsonite and potassium feldspar with dioctahedral 2:1 clay minerals; and between the sum of dawsonite and plagioclase with dioctahedral 2:1 clay (Figure 4.31).

Silicate minerals of the GRF in the PCB in order of silicon content by weight, from highest to lowest are: quartz, feldspar, analcime, and clay minerals. The order of appearance in the stratigraphic column, and increases and decreases in quantities of these silicate minerals with the addition of dawsonite, are indicative of a series related to alkalinity and silica activity. The entry into an elevated range of alkalinity and decrease in silica activity may be represented by the loss of analcime and great decrease in clay minerals and quartz, together with the increase of dawsonite and feldspar quantities at the lower transition zone in the basin center (Figures 4.4, 4.5, 4.6, and 4.8). Similarly, at the upper transition zone, dawsonite quantities greatly decrease, as analcime begins to reappear and clay minerals increase again, implying that a decrease in alkalinity has occurred (Figures 4.5, 4.6 and 4.7). The differences in character between the upper and lower transition zones imply that dawsonite is stable in chemical conditions that overlap with conditions of authigenic feldspar formation, and in conditions at which most sheet silicate minerals and analcime are no longer stable (Surdam and Parker, 1972). At the upper transition zone, feldspar quantities do not decrease again as dawsonite quantities do, but instead increase again, suggesting that related factors such as silica activity, carbonate concentrations, and/or temperature are involved in the determination of which authigenic phases form in the upper MU (Surdam and Parker, 1972; Smith, 1983; Hellavang et al. 2011). The influence of a change in silica activity at the upper transition zone is supported by the fact that quartz quantities also decrease further at the upper MU. An attempt to assess the portion of quartz present that is of authigenic origins by comparing elemental Si to Zr as a proxy for detrital input can be found in Supplemental File O.
5.4.4 Carbonate Minerals

Chemical processes are the main control on the deposition of carbonate sediments, including those of biologic origins. The carbonate system acts as a principle buffering mechanism, therefore the form of carbonate ions present in solution is dependent upon pH, playing a large role in which authigenic minerals deposited in Lake Uinta. The carbonate species bicarbonate (HCO$_3^-$) exists within the range of pH 4.5 to 12.3, and the carbonate species CO$_3^{2-}$ is present at pH 8.3 and above. The formation and stability of carbonate mineral assemblages were therefore dependent on the pH of the water column and pore waters, including calcite, aragonite, dolomite, ankerite, siderite, magnesite, and kutnohorite, as well as the saline carbonate minerals nahcolite, dawsonite, natrite, and northupite (Eugster, 1980; Boggs, 1992).

Calcium carbonate minerals in the GRF of the PCB of this study are found in much higher abundance in the basin margin section than in the basin center sections. In the middle MU of the basin center, calcite and aragonite are generally absent, and ferrodolomite is the only common Ca-Mg-Fe carbonate mineral present (Figures 4.1, 4.2, Table 4.2). Both temperature gradient and alkalinity contrasts between the layers of water likely contributed to the distribution of calcium carbonate mineral deposition in Lake Uinta sediments (Desborough, 1978). CO$_2$ is more soluble in colder water, and therefore calcium carbonate was more likely to precipitate in the warmer waters of the shallow basin margins than in colder lower layers of the deeper lake center (Eugster, 1980; Krauskopf and Bird, 1995). The low solubility of calcium carbonate at elevated pH also triggers precipitation at the basin margins as fresher fluvial waters enter the more alkaline lacustrine environment (Müller et al, 1972). Calcite readily forms in slightly basic water, and therefore a high proportion of calcium could have precipitated out of solution from freshwater runoff shortly upon entering lake Uinta on the margins of the paleobasin during more alkaline stages of the lake, preventing replenishment of calcium to the water column and deeper portions of the lake (Müller et al, 1972; Eugster, 1980; Krauskopf and Bird, 1995). During fresher stages of the stratified lake when alkalinities were not as high, calcium concentrations would not have been as depleted and could have remained higher throughout the fresher upper layer of water, so calcite and aragonite could precipitate further out into the basin (Eugster, 1980). This is evident in the fresher lake stages of the basin center in the lower and upper MUs where calcite and aragonite deposited in the basin center (Table 4.3, Figure 4.1). Inorganic
chemistry results support this, showing higher total concentrations of calcium deposited in the
tanker lake stages of the lower and upper MUs as indicated by Ca/(Ca+Mg+Fe) ratios in the
basin center sections (Figure 4.11). Early precipitation of calcium carbonate minerals leaves a
lower Ca$^{2+}$/Mg$^{2+}$ ratio in the water column, leading to higher magnesium forms of carbonate
minerals to subsequently form (Eugster, 1980; Müller et al, 1972). Dissolution of micritized
grains were recognized in samples from the basin margin Douglas Pass in the study by Surianim,
2010, which suggests that at times waters were undersaturated in calcium.

The distribution of calcium carbonate minerals in the PCB is a reflection of conditions
that allowed primary calcite and aragonite to be preserved during diagenesis. Preservation of
calcium carbonate minerals in the rock record of the GRF would occur in locations and intervals
with pore water chemistries which prevented dolomitization of primary precipitates (Müller et al,
1972; Desborough, 1978; Pitman, 1996). Buried sediments from basin margin locations, and
sediments from intervals representing fresher lake stages when stratification may have been
weaker, would contain pore waters exhibiting higher calcium concentrations. In these locations
and intervals, low-magnesium carbonate minerals were most likely to have deposited, and
magnesium would not be readily available for dolomitization of calcium carbonate minerals
(Desborough, 1978). Pore waters in the basin center, below the chemocline, would have had
lower Ca$^{2+}$/Mg$^{2+}$ ratios, deposit greater quantities of high-magnesium calcite, and have higher
iron activities due to high redox potential (Desborough, 1978; Pitman, 1996). Therefore basin
center locations would have lower calcite preservation rates, and higher concentrations of
diagenetic ferrodolomite.

Study of modern saline lakes suggests that secondary dolomite is more likely to form
when elevated levels of primary high-Mg calcite are present to be altered during diagenesis
(Müller et al, 1972; Desborough, 1978). Freshwater lakes primarily precipitate low-Mg calcite,
but modern saline lakes are known to precipitate both low-Mg calcite and high-Mg calcite, as
well as primary poorly ordered protodolomite (Boggs, 1992). Müller et al (1972) attests that in
modern saline lakes, low-Mg calcite is formed when the Mg$^{2+}$/Ca$^{2+}$ ratio is less than 2; Mg-
calcite is formed at ratios of 2 to 12; and dolomite forms at a ratio between 7 and 15 (Müller et
al, 1972). The magnesium to calcium ratio in the pore waters or lake water column is a main
control on whether primary (mainly calcite and aragonite) or secondary (mainly dolomite)
carbonate minerals form (Müller et al, 1972; Pitman, 1996). The ratio of magnesium to calcium
increases with depth in lake waters, which may provide explanation for the fact that ferrodolomite minerals are the most common in the deeper basin center of the PCB (Müller et al., 1972). Modern, freshwater lakes can have magnesium to calcium ratios of almost 2.5 times greater than that of fluvial source waters, which may be achieved by preferential concentration of Mg$^{2+}$ over Ca$^{2+}$ by cyanobacteria (blue green algae) (Müller et al., 1972; Desborough, 1978). Enrichment of Mg$^{2+}$/Ca$^{2+}$ ratios by cyanobacteria would have led to the precipitation of high-Mg calcite in Lake Uinta, and later dolomitization of primary-precipitated carbonate minerals (Desborough, 1978).

Dolomite forms from slow reactions that operate best at high pH, high salinity, elevated temperatures, and high Mg$^{2+}$/Ca$^{2+}$ ratios (Surdam and Eugster; 1976; Eugster, 1980; Deer et al., 1992; Krauskopf and Bird, 1995). Both the alkaline and highly reducing conditions of the basin center of paleolake Uinta in the PCB were likely conducive to precipitation of both primary iron-rich protodolomite and Mg-calcite, and to the subsequent alteration of primary calcite to secondary ferrodolomite post-burial (Müller et al., 1972; Desborough, 1978). Mg-calcite was detected in only trace amounts in the basin center sections in the GRF in this thesis, and at slightly higher concentrations in the basin margin section. The minor concentrations of Mg-calcite relative to calcite found in the GRF of the PCB may be due to conversion to dolomite in waters with elevated Mg$^{2+}$/Ca$^{2+}$ ratios. Occurrences of Mg-calcite were only detected in the fresher, lower MU and upper MU in both basin locations, suggesting that it may have precipitated in larger quantities originally, but almost completely converted to ferrodolomite in the more saline, alkaline middle MU (Desborough, 1978).

The modern Lake Bosumtwi in Ghana, Africa, is an analog to ancient Lake Uinta, as a saline, alkaline, restricted basin with high organic productivity (Pitman, 1996). Pitman (1996) compared geochemical trends from primary and diagenetic carbonate minerals in Lake Bosumtwi to carbonate minerals in a GRF core from the USBM 01A well in the basin center of the PCB (Figure 2.2). Diagenetic carbonate minerals in Lake Bosumtwi have high-positive $\delta^{13}$C values, and deposit in pore waters near the sediment-water interface, under a water column where methanogenic activity and evaporation rates are high (Pitman, 1996). Carbonate minerals with high-positive $\delta^{13}$C values in the PCB GRF derived from pore-water bicarbonate in organic-rich sediments, where diagenetic reactions were mediated by bacterial activity. Pore waters became more alkaline as sulfate reduction and decarboxylation of high quantities of organic
matter took place in the shallow sediments. Once sulfate had been exhausted, methanogenic bacteria dominated, which greatly influenced the isotopic composition of dissolved inorganic carbon in sediments and diagenetic carbonate minerals that precipitated (Pitman, 1996). Therefore, diagenetic carbonate minerals are found in intervals of the GRF where sediments were dysoxic or anoxic, and production of organic matter and carbon burial rates were high, when lake waters were strongly stratified (Pitman, 1996) (Figure 4.24). This suggests that ferrodolomite in the GRF is largely a diagenetic mineral, and it is present in the highest concentrations in intervals from the most alkaline, saline lake stages, when stratification was likely to be the strongest. Ferrodolomite has been shown in this thesis to be the most abundant in the basin center, where the waters would have been most ubiquitously under the chemocline.

Pitman (1996) quantified carbonate minerals in the sample suite from the USBM 01A core by measuring the ratios of dolomite/calcite XRD peak heights above background, and found that high oil yield intervals were richer in dolomitic carbonate minerals, and low oil yield intervals were richer in calcitic carbonate minerals (Pitman, 1996). Pitman’s findings are consistent with qualitative results in this thesis that show that ferrodolomite is most abundant in basin center samples where organic matter concentrations are high, and that calcite is most abundant in basin margin samples where organic matter contents are relatively lower (Figures 4.3 and 4.4). In addition, in the basin center, the highest concentrations of calcite occur in the lower MU and upper MU, which have relatively low organic matter concentrations, whereas the middle MU is rich in both organic matter and ferrodolomite, and virtually devoid of calcite (Tables 4.3, Figure 4.1). The negative correlation between calcite and organic matter, and positive correlation between ferrodolomite and organic matter, together with the basinal distributions, suggests that ferrodolomite in the PCB GRF is generally a diagenetic mineral which precipitates in anoxic sediment pore waters, when and where lake water stratification and methanogenic bacterial action was strong, as is observed in Lake Bosumtwi (Pitman, 1996).

5.4.5 Salinity

Saline carbonate and bicarbonate minerals, such as nahcolite, dawsonite, natrite and northupite are found exclusively in continental basins (Eugster, 1980). Lacustrine sediments differ from marine sediments in that the pore waters normally have much lower concentrations of dissolved ions, especially sulfate, while bicarbonates can be abundant (Boggs, 1992). This class
of minerals does not form under marine saline conditions because of the dominance of chlorine and sulfate ions in marine waters (Eugster, 1980).

In the basin center, nahcolite, dawsonite and halite are the major saline minerals, and together with plagioclase, are the major sodium-bearing minerals. This mineral assemblage is indicative of the much higher concentrations of sodium reached in the basin center than in the basin margin. In the basin margin, the main sodium-bearing minerals are the aluminosilicate minerals, plagioclase and analcime. Na/Al ratios demonstrate that sodium concentrations were up to over 50 times that of aluminum at times in the basin center, whereas aluminum concentrations were consistently over twice that of sodium in the basin margin (Figures 4.35, 4.36). It has been estimated that lake waters that deposited the GRF had become saline to hypersaline in later Stage 2 of the middle MU (Surdam and Parker, 1972; Smith et al, 2008; Tänavsuu-Milkeviciene and Sarg, 2012). The definition of saline water in most geological applications is 3 to 35 parts per thousand total dissolved solids (TDS), with hypersaline being greater than 35 0/00, and fresh as less than 3 0/00 (Last and Ginn, 2005). Some nomenclatures define saline waters as approximately the same concentration as seawater (35,000 mg/l TDS), and 1000 to 20,000 mg/l to be brackish (Drever, 1997).

As aluminosilicate minerals were degraded in increasingly alkaline conditions of Lake Uinta, less soluble cations remained in the sediments, and sodium was released in solution, where it concentrated in the lower layer of water in the basin center (Eugster, 1980; Smith, 1983; Krauskopf and Bird, 1995). Below the chemocline, excess sodium was incorporated into authigenic minerals, including plagioclase and saline minerals. Sodium concentrations in the basin center were much higher than in the basin margin, with Na/K ratios of 11.2 average, and up to a maximum of 151.1, compared to Na/K ratios in the basin margin which were much lower at 0.78 average and 2.0 maximum (Figures 4.35 and 4.36).

Comparison of inorganic chemistry to quantitative mineralogy shows that punctuated occurrences of nahcolite appear in the basin center at the same points at which sodium saturations spike (Figure 4.36). Sodium concentrations track with depth plots of nahcolite quantities in the basin center, but in the margin, sodium quantities parallel the occurrence of analcime (Figure 4.35). Sodium concentrations are a larger influence on nahcolite deposition than on plagioclase or dawsonite deposition as shown by the lack of correlations between sodium concentrations and plagioclase or dawsonite in the basin center (Figure 4.36). The formation of
nahcolite, NaHCO₃, over other sodium carbonate minerals is also dependent upon conditions within specific mineral fields defined by pCO₂ versus temperature, sodium versus chloride concentrations, and pH (Eugster, 1980; Smith et al, 1987; Lowenstein, 2011). Figure 5.4 illustrates a nahcolite saturation level being dependent upon the log[Na+activity/ H+ activity], requiring higher sodium concentrations and alkalinity than dawsonite to precipitate (Hellavang et al. 2011). The buildup of high concentrations of sodium ions in the water column and pore waters was as a consequence of the hydrolysis of aluminosilicate minerals at elevated pH, especially the breakdown of sodic feldspars (equations 5.2 and 5.3) (Eugster, 1980; Smith, 1983).

Concentrations of sodium became high enough to trigger the sudden precipitation of nahcolite from the water column in large quantities, rapidly enough that it had the effect of overwhelming all other minerals being deposited (Boak and Poole, 2014; Jagniecki and Lowenstein, 2014). This dilution effect provides a partial explanation for many of the limited exclusive relationships that nahcolite exhibits with other minerals in the saline zone assemblage, such as dawsonite and buddingtonite (Figures 4.28 and 4.27).

Smith et al. (1987) monitored the salts that crystallized during the desiccation of a modern saline lake in California, Owens Lake, which contains many sodium carbonate minerals. The pH of Lake Owens was measured at between 9.3 and 11.0, which precipitated nahcolite, halite, and other sodium carbonate minerals that did not form in the GRF of the PCB, but are found in the GRF of other basins (Dyni, 1997; Smith et al, 1987). Both nahcolite and halite precipitated as floating crystals on the surface of the water of Lake Owens as evaporative concentration increased salinity, regardless of temperature. These crystals then fell and accumulated on the basin floor (Smith et al, 1987). This supports the theory that bedded nahcolite in the GRF precipitated from the water column to accumulate thick deposits at the bottom of the paleolake, once critical salinities were reached. It is possible that crystal formation in paleolake Uinta was not at the surface of the lake above the less saline upper layer of water, but at the chemocline at the interface with the lower water layer (LaClair and Lowenstein, 2009; Lowenstein, 2011). It has been suggested that halite morphologies indicate that halite beds in the GRF also form from bottom-growth crystals (Jagniecki and Lowenstein, 2014).

The multiple morphologies of nahcolite found in the GRF of the PCB are most likely a consequence of where and when crystals precipitated. Nahcolite exists exclusively in nodular form in the leached zone in stages S4, S5 and S6 in the GRF of the PCB, while the lake was
rising, high and closing (Daub et al. 1985; Tänavsuu-Milkeviciene and Sarg, 2012). Since waters were freshening in these upper lake stages, the nodular form may be diagenetic, as a consequence of the dissolution of existing nahcolite or breakdown of other sodium and carbonate-bearing minerals in the alkaline pore waters. To form nodules or disseminated crystals, nahcolite reprecipitated at or below the sediment water interface (Jagniecki and Lowenstein, 2014). Notably, most salt phases in Lake Owens, except halite, were subsequently redissolved after initial precipitation more than once and recrystallized again (Smith et al. 1987). Study of salts in Lake Owens indicate that primary precipitates are not preserved in the rock record, and only the post-diagenetic forms of salt minerals survive (Smith et al. 1987). The two morphologies of nahcolite exhibit separate populations of δ¹³C values, which suggest that bedded nahcolite precipitated from the water column (Pitman, 1996). Low δ¹³C values in bedded nahcolite are attributed to active photosynthetic productivity, and lower δ¹³C in nodular nahcolite are correlated with methane generation in organic rich sediments (Pitman, 1996).

Dawsonite appears before nahcolite in the stratigraphic section, which may be an indication that elevated pH occurred before hypersaline conditions developed (Figures 4.5, 4.6, 4.7 and 4.8). The facts that the highest average quantities of dawsonite and nahcolite occur in separate rock types (Table 4.6) (marlstone for dawsonite, subaqueous evaporite for nahcolite), and that dawsonite and nahcolite demonstrate a limited exclusivity relationship (Figure 4.27), and the contrasts in histograms of abundance distributions suggest that dawsonite and nahcolite are saline minerals that require separate conditions of formation and have different modes of formation (Figure 4.21) (Supplemental File N). Dissolution features of leached out nodules throughout the upper MU, from the top of rich zone R5 up to R8 (S4 through S6) indicate that nahcolite deposition persisted after dawsonite ceased to form, and therefore elevated salinities may have outlasted highly alkaline conditions later in the paleolake history (Daub et al., 1985; Dyni, 1997). Dawsonite also has a greater lateral extent of deposition in the basin than nahcolite and halite, suggesting that extreme salinities occurred in a more restricted location than high alkalinity. (Beard et al, 1974; Daub et al. 1985; Dyni, 1996; Tänavsuu-Milkeviciene and Sarg, 2012). This disparity in depositional extents may also be an artifact of preservation, since halite and nahcolite are both soluble minerals, and dawsonite is not.
CHAPTER 6

CONCLUSIONS

The fine-grained nature of rock types in oil shale formations makes determination of the mineral composition an essential part of understanding the evolution of the paleo basin. The exotic mineral assemblages of the Green River Formation (GRF) are a consequence of deposition under unusually extreme conditions in a hypersaline, alkaline and reducing lacustrine environment. The water chemistry responsible for the formation of multiple authigenic phases in the GRF may have also existed to lesser degrees in other organic-rich, restricted basins. Therefore, recognition of trace quantities of similar authigenic assemblages in other deposits of oil shale, shale oil and shale gas may be considered indicators of brief periods with similar water column and pore water conditions.

1. Mineral assemblages across the basin, from deepwater, basin center to shallow, near-shore facies, are supportive of the existence of a permanently stratified saline lake consisting of two layers of water separated by a chemocline. Mineral distributions are indicative of a fresher upper water layer in contact with margin sediments, and a hypersaline, alkaline and reducing lower water layer in contact with deeper, basin center sediments.

2. Petrographic and SEM-EDS analysis provides evidence of authigenic and diagenetic origins for a large assemblage of minerals. Fine-grained, euhedral crystals, and pure end member compositions of solid solutions have been observed.

   a. The main authigenic phases in the basin center include, but are not limited to: dawsonite, buddingtonite, potassium feldspar, albite and quartz. The major chemically precipitated minerals in the basin center include, but are not limited to: ferrodolomite, nahcolite and halite.

   b. The main authigenic phase in the basin margin includes, but is not limited to: analcime. The major chemically precipitated minerals in the basin margin include, but are not limited to: calcite and ferrodolomite.
c. Original major detrital minerals included, but were not limited to: quartz, plagioclase, potassium feldspar, and clay minerals.

3. The order that authigenic and diagenetic minerals appear in the stratigraphic sections is suggestive of the order of the development of three main components of paleowater-chemistry in Lake Uinta: reducing conditions, alkalinity, and finally salinity.

4. Stratigraphic variations in mineral assemblages are supportive of the basin evolution constructed for the GRF in the PCB with sequence stratigraphy by Tänavsuu-Milkeviciene and Sarg (2012). In general, lake history is confirmed by geochemical conditions of the depositional environments indicated by the distribution of preserved mineral phases.

5. The quantification of a comprehensive suite of minerals, in a formation with high concentrations of unusual authigenic minerals such as the GRF of the PCB, permits detailed study of the conditions of their formation and depositional environment. In lacustrine or other restricted basin settings where sustained periods of extreme geochemical conditions were not maintained, even trace occurrences of minerals described here may be interpreted to signify a brief period of elevated alkalinity, salinity, and/or lowered redox potential.

6. An integration of 4 sets of data presented in this thesis leads to the interpretation of general geochemical significances for identified minerals. These data include mineral relationships (linear, mutually exclusive, and limited exclusive plots); conditions of authigenic formation (from laboratory synthesis, literature and chemical properties); basin distributions (areal extents of saline deposition, basin margin vs center); and stratigraphic distributions (mineral units, transition zones, and order of appearance).

   a. Reducing conditions: indicating dysoxia and anoxia
      i. Buddingtonite, Ferrodolomite, Siderite

   b. Alkaline conditions: in order of indicating increasing pH
      i. Calcite, Aragonite, varied clay mineral types, Quartz:Feldspar ratio >2 →
      ii. Analcime, dominance of dioctahedral 2:1 Clay minerals, increased high-iron Dolomite, Quartz:Feldspar ratio <2 →
      iii. Dawsonite, authigenic Feldspars
c. Salinity: in order indicating higher sodium concentrations:
   i. Analcime and authigenic Albite → Dawsonite → Nahcolite → Halite

d. High Mg/Ca ratios: (between 7 and 12) Dolomite

e. Fe/Ca ratio over 0.05: Siderite

f. Si/Al ratios: high to low: Analcime → Quartz;

g. Silica activity: high to low: Feldspar → Analcime → Dawsonite
CHAPTER 7
FUTURE WORK

Optimal samples for XRD work aimed at understanding authigenic mineral origins should be of small size that ideally only takes rock from within one bed to represent as homogenous an environment of deposition as possible. Quantitative relationships between minerals and higher coefficients of determinations may be obtainable to verify the qualitative trends identified here if samples are longer width-wise than vertically, taken along a thick lamination, avoiding nodules or other visible heterogeneity. The approximate two inch height of core used in this study is a large enough interval to introduce error in quantitative proportions between minerals, due to sampling of multiple laminations with distinct mineral assemblages, representing multiple conditions of deposition.

1. A sequence of minerals have been identified here which can be used as geochemical tools to estimate the alkalinity of paleolake bottom waters. Similarly, further research should be employed for the construction of paleoredox and paleosalinity mineral sequences with assigned quantitative values. Quantitative redox values would be useful for buddingtonite and ferrodolomite. Quantitative pH values would be useful to apply to clay mineral types. In addition, a finer understanding of alkalinity and reducing conditions would be facilitated by a more detailed study distinguishing between dolomite, ferroan dolomite and ankerite.

2. Redox conditions as determined by the use of V/Cr ratios has limitations and has been adapted for use here from the original application in marine mudstone (Jones and Manning, 1994). Future work should also look at multiple other paleoredox indicators such as Ni/Co or degree of pyritization (Jones and Manning, 1994).

3. Further petrographic study is warranted for identification of alteration fabrics and evidence of replacement. Paragenetic analysis would be useful to describe the order of deposition for secondary minerals and their modes of emplacement (as cement etc.). A quantitative evaluation which included many more thin sections than used in this study might be able to determine the proportion of authigenic versus detrital phases in the basin center.
4. Clay mineral XRD separates should be prepared for the purpose of distinguishing between dioctahedral 2:1 clay mineral types illite, smectite, mixed layer illite/smectite, and muscovite; and to identify the individual members within the category of trioctahedral 2:1 minerals. Investigation into the stratigraphic clay type distribution may give insight into depositional conditions, weathering reactions and diagenetic alteration.

5. Future work should include reevaluation of all 82 XRD sample patterns using JADE software, in order to employ the more comprehensive database of minerals. A more detailed evaluation of the complete mineral assemblage which integrates all minor minerals may give a better understanding of the history of the paleobasin, such as the identification of precursor minerals which may have been almost completely altered.

6. Applying multivariate statistical techniques, such as principle component analysis (PCA), or cluster analysis would provide a quantitative statistical assessment of the relationships between minerals and assist in compressing many variables into key parameters. These statistical techniques may help to delineate the differences in assemblages between basin locations and lake stages, and create groupings which provide clarification of the lake’s chemical evolution above and below the chemocline.

7. For more definite determinations of authigenic vs. detrital origins of silicate phases, the addition of cathodoluminescence or ion probe analysis is recommended in conjunction with optical petrographic and SEM analysis with this set of samples. (Boggs, 1992).
REFERENCES


• Boak, J., and Poole, S. Mineralogy of the Green River Formation in the Piceance Creek Basin, Colorado, in Stratigraphy and Limnogeology of the Eocene Green River Formation, Springer-Verlag, accepted for publication, expected end 2014.


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• Malicse, A., 2011. Mineralogy and Geochemistry of the Parachute Creek Member of the Green River Formation, Piceance Basin, Colorado, USA. Search and Discovery Article


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# APPENDIX A
## LIST OF SUPPLEMENTAL FILES

### MINERAL AND CHEMICAL DATA

Quantitative XRD and Inorganic and Organic Chemistry Results in Excel Spreadsheets. See Chapter 3 METHODS, DATASETS AND DATA QUALITY for descriptions of analyses.

<table>
<thead>
<tr>
<th>Supplemental File</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SUPPLEMENTAL FILE A</strong>&lt;br&gt;Bulk XRD Basin Margin Quantitative Results Table.xlsx</td>
<td>Table of Bulk XRD Quantitative Mineral Results for the Basin Margin of the Douglas Pass Outcrop Samples</td>
</tr>
<tr>
<td><strong>SUPPLEMENTAL FILE B</strong>&lt;br&gt;Bulk XRD Basin Center Quantitative Results Table.xlsx</td>
<td>Table of Bulk XRD Quantitative Mineral Results for the Basin Center for the John Savage 24-1 and Shell 23X-2 Core Samples. Normalized with and without Organic Matter. Includes Integrated Chevron ETC Analysis, JADE Analysis, and ExxonMobil USGS Data</td>
</tr>
<tr>
<td><strong>SUPPLEMENTAL FILE C</strong>&lt;br&gt;XRD CR-2 SemiQuantitative Data Table.xlsx</td>
<td>Table of Original CR-2 Core XRD Data Measured from Peak Heights Digitized for this Project from the Work of Dean, Pittman &amp; Harrach (1981).</td>
</tr>
<tr>
<td><strong>SUPPLEMENTAL FILE D</strong>&lt;br&gt;Chemistry Data Table.xlsx</td>
<td>Table of Results of Chemical Analysis and Activation Lab Method Specifications</td>
</tr>
</tbody>
</table>

### XRD PATTERNS

Raw Spectra for Each Sample Analyzed at Chevron ETC Labs. Includes Quality Control Testing Done for Sample Preparation and Software Analysis. See Chapter 3 METHODS, DATASETS AND DATA QUALITY for descriptions of analyses.

<table>
<thead>
<tr>
<th>Supplemental File</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td><strong>SUPPLEMENTAL FILE E</strong>&lt;br&gt;XRD Patterns Basin Center Samples. pdf</td>
<td>Compilation of John Savage 24-1 and Shell 23X-2 Basin Center Raw XRD Patterns for Samples Analyzed at Chevron ETC</td>
</tr>
<tr>
<td><strong>SUPPLEMENTAL FILE F</strong>&lt;br&gt;XRD Patterns Quality Control and JADE Analysis. pdf</td>
<td>Compilation of John Savage 24-1 Basin Center XRD Patterns of samples Reanalyzed with JADE; Before and After Additions of Internal Standard with Chevron’s Software; and Ball Milled Samples Before and After McCrone Milling, etc</td>
</tr>
<tr>
<td><strong>SUPPLEMENTAL FILE G</strong>&lt;br&gt;XRD Patterns Basin Margin Douglas Pass Samples. pdf</td>
<td>Compilation of Douglas Pass Outcrop Basin Margin Raw XRD Patterns for Samples Analyzed at Chevron ETC</td>
</tr>
</tbody>
</table>
PHOTOGRAPHS OF SAMPLES

See Chapter 3 METHODS, DATASETS AND DATA QUALITY for descriptions of sampling in section 3.1 Sample Selection and Locations. See figure 2.2 for a map of the locations of sections. See table 3.1 for a summary of the number of each samples from each section in this study.

| SUPPLEMENTAL FILE H | Photos of Core Samples Shell 23X-2.pdf | Shell 23X-2 Core Sample Photos with Rock Type Descriptions |
| SUPPLEMENTAL FILE I | Photos of Core Samples JS 24-1.pdf | John Savage 24-1 Core Sample Photos with Rock Type Descriptions |
| SUPPLEMENTAL FILE J | Photos of Outcrop Samples Douglas Pass.pdf | Douglas Pass Outcrop Sample Photos with Rock Type Descriptions |

ADDITIONAL ANALYSES AND INTERPRETATIONS

Expanded Material, and Figures and Calculations not Included in the Main Text

| SUPPLEMENTAL FILE K | Clay Mineral CEC Summary Table.xlsx | Table of Cation Exchange Capacity (C.E.C.) Results for Clay Mineral-Rich Samples. See Figure 4.19 |
| SUPPLEMENTAL FILE L | Organic Matter Comparison by Method.pdf | Comparison of quantitative results of total organic carbon (TOC) by source rock analysis (SRA), organic carbon (Corg) by infrared spectroscopy (IR), and organic matter by XRD. See Section 4.5.6 |
| SUPPLEMENTAL FILE M | Qualitative Relationships of Selected Authigenic Phases.pdf | Qualitative Depth Plot Relationships Between and Amongst Major Authigenic Minerals of the Basin Center: Buddingtonite, Dawsonite, Plagioclase, Potassium Feldspar, and Quartz. See Section 4.7 Mineral Relationships |
| SUPPLEMENTAL FILE N | Rock Type Results Table.xlsx | Table of Sample Rock Type Classifications Including Grain-Size, Mineralogy, and Facies for Each Sample. See Section 4.8, Tables 4.4, 4.5 and 4.6, and Figures 4.38, 4.39, 4.40 and 4.41. |
| SUPPLEMENTAL FILE O | Quartz Origin Zr Proxy Detrital vs Authigenic.pdf | The Relationships Between Si And The Detrital Source Proxy, Zr, in Attempt To Estimate The Fraction Of Quartz Which Formed As An Authigenic Phase. See Discussion Chapter 5.4.3 Na-Al Minerals |
| SUPPLEMENTAL FILE P | Tables of Lake Stage Quantitative XRD Results.pdf | Average Wt% Concentrations Of Major Mineral Phases By Lake Stage for the Basin Margin and Basin Center. See Table 4.3 and Discussion Section 5.3 Mineral Units |
| SUPPLEMENTAL FILE Q | Enlarged version of Figure 2.4 Correlation between Basin Margin and Basin Center Sections including the John Savage 24-1, Shell 23X-2, Douglas Pass Outcrop Sections and comparison well Colorado-1 |
| SUPPLEMENTAL FILE R | Enlarged version of Figure 4.5 CO-1 depth plots for 8 minerals, from semi-quantitative relative peak heights measurements by XRD, Fischer Assay and resistivity profiles |
| SUPPLEMENTAL FILE S | Enlarged version of Figure 4.6 CR-2 depth plots for 11 minerals, from semi-quantitative relative peak height measurements by XRD |
| SUPPLEMENTAL FILE T | Enlarged version of Figure 4.7 John Savage 24-1 depth plots with quantitative values for 12 minerals from the upper basin center section. Blue line marks upper transition zone. Lake stages, rich zones shaded gray, lean zones in white, and Fischer Assay profile marked on the left vertical axis. Legend gives facies associations in stratigraphic column of basin center John Savage 24-1 and Shell 23X-2 cores, modified from Tännavsuu-Milkeviciene and Sarg, (2012) |
| SUPPLEMENTAL FILE U | Enlarged version of Figure 4.8 Shell 23X-2 quantitative values for 12 minerals from the lower basin center section. Blue line marks lower transition zone. Lake stages, rich zones shaded in gray, lean zones in white, Fischer Assay and gamma ray profiles on left vertical axis. Legend for facies of stratigraphic column in Supplemental File F, modified from Tännavsuu-Milkeviciene and Sarg, (2012) |
| SUPPLEMENTAL FILE V | Enlarged version of Figure 4.9 Douglas Pass quantitative values for 13 minerals from the basin margin. Lake stages, rich zones shaded gray, lean zones in white, gamma ray profile on left vertical axis. Facies associations of stratigraphic column of basin margin given in legend in Fig. 4.9, modified from Tännavsuu-Milkeviciene and Sarg, (2012) |