

CHEMOSTRATIGRAPHIC APPLICATIONS TO LOW-ACCOMMODATION FLUVIAL INCISED-VALLEY SETTINGS: AN EXAMPLE FROM THE LOWER MANNVILLE FORMATION OF ALBERTA, CANADA

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ABSTRACT: Incised valleys are a ubiquitous feature of the Lower Cretaceous Mannville Group of the Western Canada Sedimentary Basin. The Basal Quartz, a member of the Lower Mannville Formation, is present in two north–south-oriented subparallel valley-form systems in southern Alberta, the western valley form termed the Taber–Cutbank Valley and the eastern valley form termed the Whitlash Valley. This paper details the application of chemostratigraphy to discriminate between the three informal lithostratigraphic units of the Basal Quartz, namely the Horsefly, the Bantry–Alderson–Taber (BAT), and the Ellerslie units in these valley forms.

In the Taber–Cutbank Valley, the Horsefly, BAT, and Ellerslie units each have unique chemostratigraphic signatures that enable them to be readily differentiated using inorganic geochemical data. The changes in elemental chemistry that allow this differentiation are inferred to reflect changes in sediment provenance, paleoclimate, and surface residence time. The whole-rock geochemistry of the Horsefly unit, the basal unit of the fill, is demonstrated to remain relatively constant longitudinally in the Taber–Cutbank Valley, therefore demonstrating, when compared to the vertical changes in geochemistry, that temporal or stratigraphic changes are of a greater magnitude than longitudinal changes within in a single valley form.

The whole-rock geochemistry of the Horsefly unit in the two valley forms, which in previous studies has been demonstrated to be homotaxial by conventional stratigraphic techniques, is markedly different between the two valley forms. The geochemical differences suggest that the Horsefly unit was subjected to more prolonged and/or intense weathering in the eastern Whitlash Valley than in the western Taber–Cutbank Valley, and that the provenance of the Horsefly unit is fundamentally different between the two valley systems.

The application of chemostratigraphy to the Basal Quartz of the Lower Mannville Formation demonstrates that the technique can be utilized as a viable correlation tool in low-accommodation incised-valley settings; however, it is most effective when the whole-rock geochemical data are placed in a regional context by integration with a detailed stratigraphic framework. Once chemostratigraphy is used in conjunction with these other data streams, the differences in geochemistry of the Horsefly unit between the Whitlash and Taber–Cutbank Valleys can be used to infer that the Horsefly unit deposited in the two valleys are two homotaxial, not coeval subunits.

INTRODUCTION

Sedimentation is governed by the rate of sediment flux supplied to a depositional system and the rate at which space is made available for potential sediment accumulation (termed “accommodation” by Jervey 1988). Numerous stratigraphic techniques are employed in order to correlate sedimentary units in various accommodation settings (e.g., sequence stratigraphy, allostratigraphy, lithostratigraphy, etc.). Chemostratigraphy is another potential technique that can be employed in order to objectively characterize stratigraphic units, and is defined as “the development of stratigraphic frameworks using inorganic whole-rock geochemical data” (Pearce 1991). Chemostratigraphy has been demonstrated to be a valid stratigraphic technique in moderate- to high-accommodation fluvial settings (e.g., Pearce et al. 1999; Pearce et al. 2005a; Pearce et al. 2005b; Ratcliffe et al. 2006; Ratcliffe et al. 2010). The work of those authors on the Barren Red Measures of the Southern

North Sea (Pearce et al. 1999; Pearce et al. 2005a; Pearce et al. 2005b), the TAG-I of Algeria (Ratcliffe et al. 2006), and the Mungaroo Formation on the NW Shelf of Australia (Ratcliffe et al. 2010) have shown that coeval homotaxial lithostratigraphic units preserve their geochemical signature over tens of kilometers in moderate- to high-accommodation settings. Therefore, temporal or stratigraphic changes in whole-rock geochemistry similar to those identified in the Triassic Mungaroo Formation (Ratcliffe et al. 2010) can be used to build a chemostratigraphic framework that can be correlated throughout the Gorgon Field, a maximum distance of 50 km. However, as outlined below, low-accommodation fluvial settings present a set of different challenges when applying any stratigraphic technique, including, as demonstrated in this paper, chemostratigraphy.

Low-accommodation, nonmarine, incised-valley depositional settings, such as those occurring during the Early Cretaceous of the southern Western Canada Sedimentary Basin (WCSB), commonly contain significant oil and gas accumulations, resulting in numerous publications

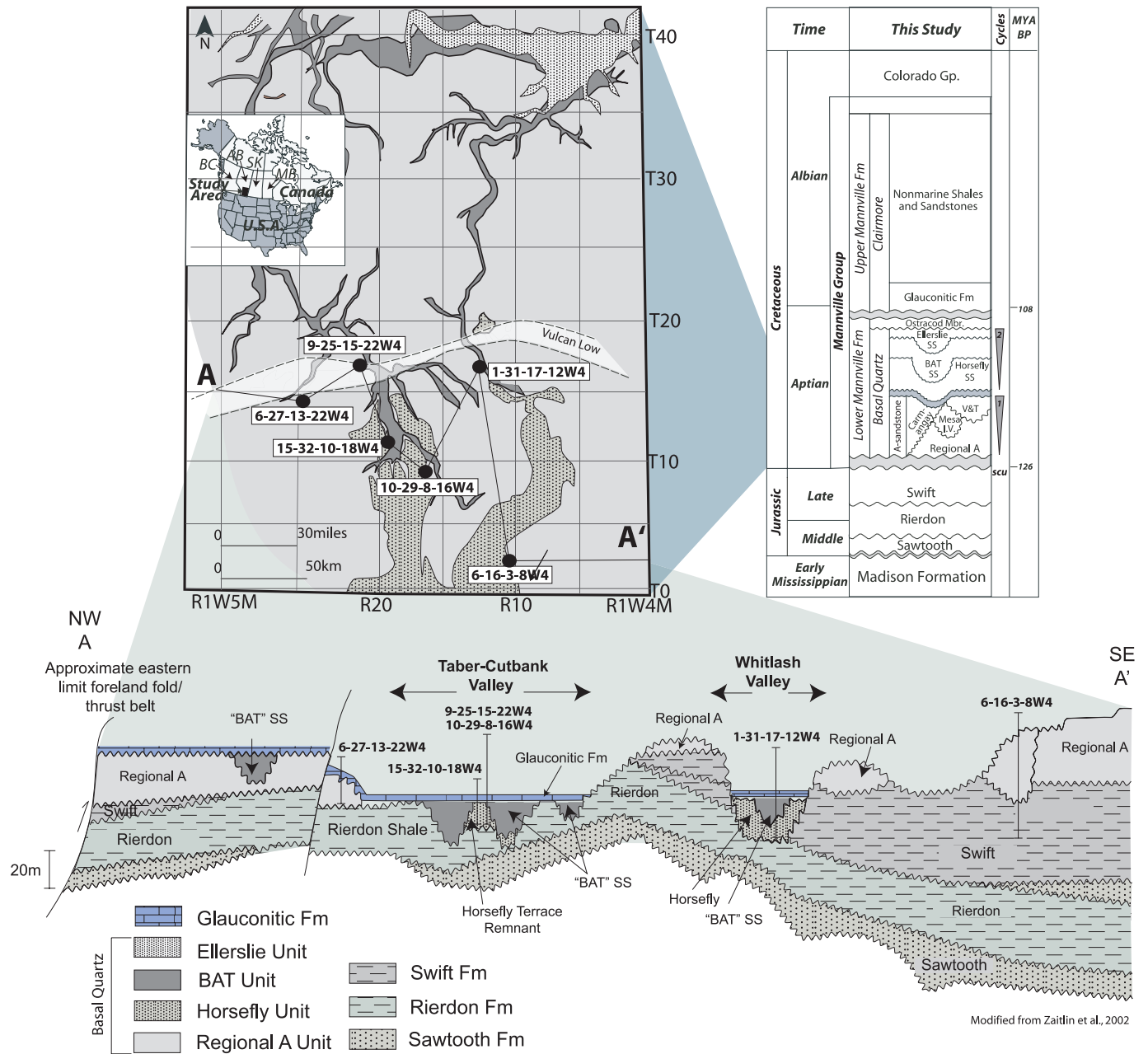


FIG. 1.—Top left. Study area location with the distribution of the Horsefly, BAT, and Ellerslie units in southern Alberta (modified from figure 30 in Zaitlin et al. 2002). Inset map indicates study area in relation to North America (BC = British Columbia; AB = Alberta; SK = Saskatchewan; MB = Manitoba). A–A' indicates line of section for cross section; Top right stratigraphic column, modified from figure 1 in Zaitlin et al. 2002. A Sandstone (including Regional A, Carmangay, Mesa Incised Valley (I.V.), A Valley and Terrace (V&T), Horsefly Sandstone (SS), BAT SS (Bantry–Alderson–Taber), and Ellerslie SS are informal stratigraphic units described in Zaitlin et al. (2002). Cycles 1 and 2 refer to mineralogical and textural cycles described in Zaitlin et al. (2002). Geologic ages from Gradstein et al. (1996). Gp = Group; Fm = Formation; Mbr = Member; SCU = Sub-Cretaceous unconformity; Lower diagram is a northeast–southwest schematic cross section (A–A' on top left map) displaying the distribution of Basal Quartz units in southern Alberta (modified from figure 30 in Zaitlin et al. 2002) and specifically the homotaxial nature of the Horsefly unit between the Taber–Cutbank Valley and the Whitlash Valley.

attempting to better understand their complex stratigraphy (e.g., Zaitlin and Shultz 1984; Brown 1993; Zaitlin et al. 2002; Dalrymple et al. 2006; Deibert and Camilleri 2006). The Lower Mannville Formation can overall be considered *accommodation-limited*, a situation in which long-term subsidence rates are low compared to sediment supply. In the study area, south of Township 35 (Fig. 1), the formation was deposited under *extremely low accommodation*, with isopach values between 0 and 40 m and net sedimentation rates < 2.2 m/Myr (Zaitlin et al. 2002).

In a sequence stratigraphic context, accommodation-limited settings promote the preservation of lowstand-system-tract deposits. The lowstand deposits are preferentially preserved in stratigraphic lows, such as the base of incised valleys. Transgressive deposits have potential for preservation if deposited in backfilling incised valleys. Thin highstand deposits are more subject to removal by subsequent cycles of erosion. The basic sequence stratigraphic correlation surface in terrestrial settings is the sequence boundary, located at the base of incised valleys and laterally

correlated onto the interfluvial (Zaitlin et al. 1994). In active tectonic areas, like the WCSB in the Early Cretaceous, variations in basin geometry and source area promoted variations in sediment composition between incised-valley systems.

Incised valleys are a characteristic basin response to tectonic or eustatic lowering of base level (Dalrymple et al. 1994; Rossetti 1998; Rossetti and Junior 2004) creating low-accommodation settings (see Zaitlin et al. 1994; Boyd et al. 2006 for a full discussion) and are a ubiquitous feature of Lower Cretaceous sedimentation of the WCSB (e.g., Cant and Abrahamson 1994; Hayes et al. 1994; Leckie et al. 1997; Leckie et al. 2004; Zaitlin et al. 2002; Boyd et al. 2006). Understanding the stratigraphy of incised-valley systems enhances our knowledge of the geological history of an area, including evidence of sea-level change, episodic tectonic uplift or subsidence, and climate change (e.g., Van Wagoner et al. 1990; Zaitlin et al. 1994; Boyd et al. 2006; Dalrymple et al. 2006; Strong and Paola 2008). However, developing robust nonmarine stratigraphy has traditionally been difficult (e.g., Zaitlin et al. 1994; Zaitlin et al. 2002; Boyd et al. 2000); biostratigraphic control is frequently lacking, and palynological data are sparse due to the highly oxidizing environment. The polyphase erosion and deposition inherent in low-accommodation settings results in closely spaced or amalgamated sequence boundaries, thereby creating compound incised-valley systems in which marker beds are discontinuous and apparently similar rock units of markedly differing ages are juxtaposed.

In the low-accommodation portion of an underfilled axial drainage system of a foreland-basin setting, homotaxial valley forms are commonplace (e.g., Boyd et al. 2000). Homotaxial valley forms are "composed of rock stratigraphic units found to be in similar position that are not contiguous, and due to their distribution in discrete (sub-) basins exhibit their own unique sedimentation patterns and depositional history" (Zaitlin et al. 2002). These homotaxial rock-stratigraphic units also exhibit considerable variation in reservoir quality, recovery factor, oil quality, and performance characteristics that appear to be stratigraphically controlled (e.g., Arnott et al. 2000; Arnott et al. 2002; Zaitlin et al. 2002).

In this paper, the utility of chemostratigraphy to low-accommodation incised-valley depositional settings is investigated. Specifically, by considering both the longitudinal variation in geochemistry of the Horsefly unit in a single valley form, and subsequently comparing the geochemistry of the same unit between two parallel valley forms, the paper attempts to demonstrate how chemostratigraphy can be used to evaluate the difference between coeval and homotaxial deposits, and therefore demonstrates that chemostratigraphy is a tool that can be employed to better define and correlate depositional units in low-accommodation incised-valley settings.

REGIONAL BACKGROUND

The Lower Cretaceous sedimentary rocks of the WCSB were deposited in a NNW–SSE-trending, underfilled foreland trough that developed in response to accretion and loading of the continental margin to the east (e.g., Leckie and Smith 1992; Cant 1996; Zaitlin et al. 2002). The Mannville Group rests unconformably on Jurassic deposits of the marine Swift and Rierdon formations (Fig. 1). In southern Alberta, the Mannville Group is divided into the Lower and Upper Mannville formations, with the Lower Mannville Formation comprising the undifferentiated Basal Quartz and Ostracod Member, and the Upper Mannville Formation comprising the Glauconitic Formation and undifferentiated nonmarine mudstones and sandstones underlying the Colorado Group (Fig. 1).

An isopach map constructed for the Lower Mannville Formation between the Jurassic unconformity and the Ostracod Member (Fig. 2; Cant and Abrahamson 1994; modified in Zaitlin et al. 2002) exhibits the

major depositional trends across the WCSB. There is a pronounced thickening toward the northwest, and three north–south paleodrainage systems (Spirit River, Edmonton Channel, and McMurray from west to east), defined on the basis of a > 75 m isopach map, exist north of Township 35 (Fig. 2). In the study area south of the Vulcan Aeromagnetic Low (Ross et al. 1997), or "Hinge Line" (Zaitlin et al. 2002), total thickness for the Lower Mannville Formation is generally less than 50 m and definition of paleodrainage systems using isopachs alone becomes problematic. The major controlling factors on north–south isopach variation in the Lower Mannville have been proposed as: (1) an eastern zone underlain by a series of Devonian salt-collapse features locally controlling accommodation patterns; (2) a central zone dominated by erosional paleotopography with underlying changes in basement terranes controlling accommodation; and (3) a western zone dominated by tectonic subsidence and rapidly increased accommodation in the foredeep adjacent to the fold-thrust belt (Zaitlin et al. 2002).

As was noted by Zaitlin et al. (2002), significant problems occur when attempting to assign ages to the Lower Mannville succession in southern Alberta due to an absence of usable paleontological material in the predominantly oxidized terrestrial deposits. The main Sub-Cretaceous Unconformity (SCU in Fig. 1) has variously been dated as (1) Berriasian (~ 135 Ma) to Tithonian (~ 140 Ma) in the southern WCSB foothills (Leckie and Krystinik 1995; Leckie et al. 1996; Leckie et al. 1997; Leckie et al. 2004; White and Leckie 1999) or (2) Kimmeridgian (~ 143 Ma) to Hauterivian (~ 126 Ma) in south-central Saskatchewan (Leckie et al. 1997). The amount of time absent across the SCU therefore ranges between 17 Myr and 5 Myr. The age of the Ostracod Member is generally taken as Aptian (~ 108 Ma). The time available for deposition of the Lower Mannville Formation therefore ranged from 35 Myr and 17 Myr west to east across the study area. Using the present-day preserved thickness (neglecting erosion and compaction) of 0–120 m, and the approximate duration of deposition, the net sedimentation rate for the Lower Mannville can be estimated as 6.6 m/Myr (Zaitlin et al. 2002). Thus, during deposition of the Lower Mannville Formation, the study area was considered to be accommodation-limited, i.e., long-term subsidence rates are low compared to sediment supply.

The study area south of the Vulcan structure (Fig. 1) was an area of extremely low to low-immediate accommodation. Along the Saskatchewan–Alberta border, isopach values range between 0 and 40 m thick and sedimentation rates are estimated to be less than 2.2 m/Myr (Zaitlin et al. 2002). This area, containing the Whitlash Valley (Fig. 1), is characterized by long periods of erosion and exposure and the development of mature paleosols. The Taber–Cutbank Valley toward the west with isopach values between 40 and 120 m, (Fig. 1) is characterized by net sedimentation rates between 1.3 and 6.6 m/Myr and is interpreted as having low–intermediate accommodation.

The development of the informal stratigraphic framework for the Lower Mannville Formation in southern Alberta by Zaitlin et al. (2002) was based on 9000+ wells organized into 88 regional cross sections, numerous hydrocarbon reservoir studies, > 1350 cores, and > 750 petrographic thin sections. Based on this data set, Zaitlin et al. (2002) divided the Basal Quartz into two depositional cycles, with both cycles displaying upward-increasing textural and mineralogical maturity. The younger cycle was further subdivided based on variations in mineralogy and petrophysical analysis (Fig. 3), into three informal lithostratigraphic units, namely the Horsefly at the base, the Bantry–Alderson–Taber (BAT), and uppermost Etherslie units (Fig. 1). Subsequent studies by Ratcliffe et al. (2002) and Ratcliffe et al. (2004) demonstrated that each of these informal units of the second cycle of the Basal Quartz is a distinctive chemostratigraphic unit, thereby supporting the proposed lithostratigraphic work of Zaitlin et al. (2002).

The Horsefly unit consists of repeated fining-upward successions on the decimeter to meter scale of conglomerate to pebbly braided-fluvial to

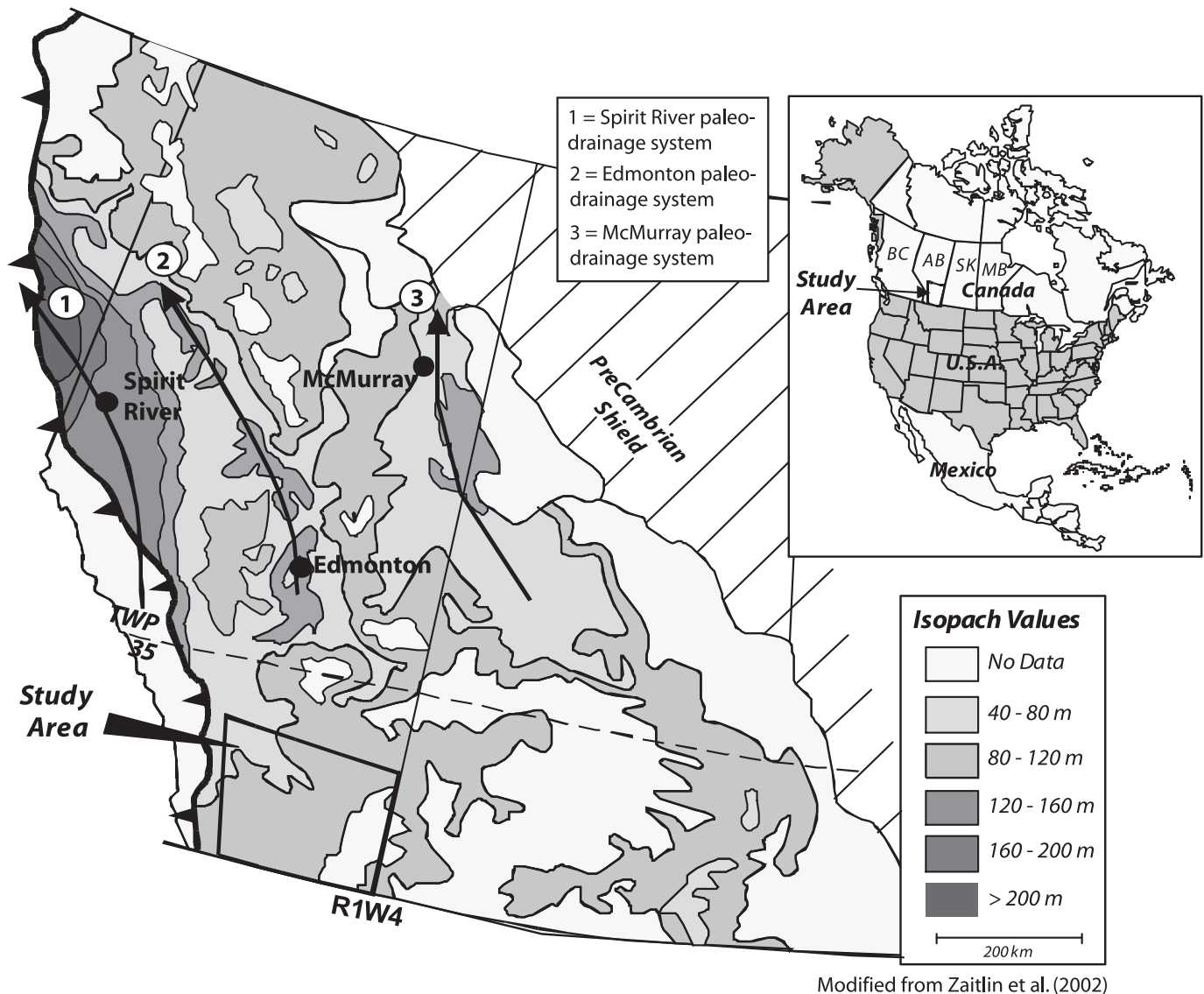


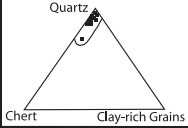

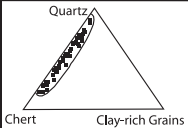
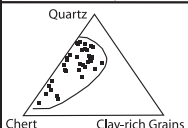
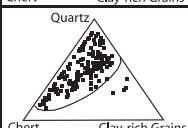
FIG. 2.—Isopach map of the Lower Mannville Formation in the WCSB, approximately equivalent to the Basal Quartz and Ostracod Member, modified from figure 2 in Zaitlin et al. (2002). Arrows indicate paleodrainages of the (1) Spirit River, (2) Edmonton and (3) McMurray systems. Inset map same as that in Figure 1.

coarse-grained meander sandstones that pass upwards into variegated paleosols, as shown in well 2-4-1-17W4 (Fig. 4). The Horsefly unit is differentiated from the underlying older A Sandstone unit and the younger overlying BAT unit by the occurrence of feldspars and cherts (Fig. 3; Zaitlin et al. 2002). Chert grains in the Horsefly (and BAT) unit(s) frequently contain pyritic inclusions and are darker in color relative to the lighter-colored chert grains in the A Sandstone (Fig. 3). The sandstone lithologies of the Horsefly unit are also characterized by an absence of carbonaceous material in comparison to the sandstones of the overlying BAT unit. The BAT unit consists of light-gray to brown, fine- to coarse-grained, moderately sorted to moderately well sorted quartz- and dark chert-bearing cross-bedded to ripple-laminated sandstones and may contain abundant carbonaceous debris, north of Township 5 (Fig. 1). The BAT unit is characterized by insignificant amounts of ductile clay-rich sedimentary rock fragments and essentially no K-feldspar (Fig. 3; Zaitlin et al. 2002). The sandstones of the Ellerslie unit commonly are fine grained, well to very well sorted, and quartz-dominated. They contain

very minor amounts of potassium feldspar and little to no dark-colored chert (Zaitlin et al. 2002).

In the study area, regional mapping has shown that the Horsefly unit was deposited in two major compound incised-valley systems: the eastern Whitlash Valley and the western Taber–Cutbank Valley (*sensu* Zaitlin et al. 1994; Zaitlin et al. 2002) (Figs. 1, 5). The total Horsefly unit succession, which is up to 25 m thick with valley forms on the order of 10–50 km wide (Figs. 1, 5), has been the focus of detailed hydrocarbon-reservoir studies in the western Taber–Cutbank Valley (e.g., Arnott et al. 2000; Arnott et al. 2002; Lukie et al. 2002). The overlying BAT unit can be divided into two sub-units based on depositional style: low-accommodation BAT (< 30 m thick) south of the Vulcan Low (Fig. 1), with a valley width of 1–5 km, and high-accommodation BAT (up to 100 m thick) to the north of the Vulcan Low with a valley width of 6–10 km.

The Ellerslie unit is characterized by high accommodation in the northern limit of the study area, and can exceed 75 m in thickness. The

Stratigraphic Nomenclature	Rock Type	Overall mineralogical & textural maturity	Diagnostic framework grains and key alteration features														
			Framework Grains	Provenance						Early diagenetic							
				Potassium Feldspar	Plagioclase Feldspar	Schistose mudrock	Anomalously large mono quartz	Glauconite	Camibalsed glauconite	Carbonaceous matter	Pyrite and dark brown chert	Orange chert	Tripolitic chert	Pelagosol (orgillans)	Spicero-siderite		
Ellerslie			■	Rare													
BAT (Bantry-Alderson-Taber)				Rare					■								
Horsefly										■							
A Sandstone				Rare													

Modified from Zaitlin et al. (2002)

FIG. 3.—Summary of compositional changes within the Basal Quartz. Modified from figure 5 in Zaitlin et al. (2002).

Ellerslie is composed of multiple stacked estuarine filled valleys (< 3 km) and deeply incised (up to 30 m), encased in bayfill interbedded bioturbated sandstone and mudstones (Zaitlin et al. 2002). The reader is referred to the paper by Zaitlin et al. (2002) for a detailed characterization of the Horsefly, BAT, and Ellerslie units.

METHODOLOGY AND DATA SET

Chemostratigraphy involves the use of major-element and trace-element geochemistry for the characterization and correlation of strata. The elemental composition of sediments is highly variable due to source composition, facies, paleoclimate, and diagenesis (see Ratcliffe et al. 2007 and references cited therein for additional discussion). The technique has been extensively used in the petroleum industry to help define stratigraphic correlations (Ehrenberg and Siring 1992; Racey et al. 1995; Preston et al. 1998; Pearce et al. 1999; Pearce et al. 2005a; Pearce et al. 2005b; Ratcliffe et al. 2006). These studies are from relatively high-accommodation settings compared to the accommodation-limited areas of Lower Mannville Formation deposition in southern Alberta.

For this study, a total of eighty-six sandstone samples were analyzed using inductively coupled plasma optical emission (ICP-OES) and mass spectrometry (ICP-MS), following a Li-metaborate fusion procedure (Jarvis and Jarvis 1992). These preparation and analytical methods provide data for 10 major elements (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, MnO, CaO, Na₂O, K₂O, P₂O₅), 25 trace elements (Ba, Be, Co, Cr, Cs, Cu, Ga, Hf, Mo, Nb, Ni, Pb, Rb, Sc, Sn, Sr, Ta, Tl, Th, U, V, W, Y, Zn, and Zr) and 14 rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Dy, Er, Tm, Yb, and Lu). Precision error for the major-element data is generally better than 2%, and is around 3% for the data on high-abundance trace elements derived by ICP-OES (Ba, Cr, Sc, Sr, Zn, and Zr). The remaining trace elements are determined from the ICP-MS and data are generally less precise, with precision error in the order of 5%.

Accuracy error is ± 1% for majors and ± 3 to 7 ppm for trace elements, depending on abundance. Expanded uncertainty values (95% confidence) which incorporate all likely errors within a statistical framework derived from 11 batches of 5 certified reference materials (CRMs), each prepared in duplicate, are typically 5–7% (relative) for major elements and 7–12% (relative) for trace elements. The ICP OES and MS facility that produced the data presented here was granted laboratory quality system accreditation to ISO 17025:2005, which is equivalent to the ISO 9000 series but focused on laboratory total quality systems.

The sandstone samples analyzed are 2 cm³ chips taken from conventional cores in wells 15-32-10-18W4, 15-32-8-16W4, 10-29-8-16W4, 7-36-8-9W4, 2-29-7-11W4, 8-34-3-11W4, and 4-5-1-9W4 (Table 1; Fig. 5). These wells were chosen for analysis because they were part of the pre-existing regional work presented in Zaitlin et al. (2002). The cored intervals had already been assigned to the Basal Quartz lithostratigraphic interval (Table 1, Fig. 5).

Figure 5 shows the sample locations in each well. When sampling core, a 2–3 cm³ chip that is typical of the parent lithology is selected, i.e., any visually anomalous features, such as concretions, fractures, mud clasts, basal lags, etc., are avoided. Any surface contamination is removed and the sample ground to a fine powder using agate mills prior to Li-metaborate digestion. An average sample spacing of approximately 0.5 m was used through the thicker sandstone packages, although the uneven sample spacing seen in Figure 5 results from attempting only to sample “average” sandstones, as discussed above, and in places poor core recovery. Similar sampling strategies were employed by Ratcliffe et al. (2002), Ratcliffe et al. (2004), and Ratcliffe et al. (2006).

Following the procedures of Pearce et al. (2005a), Ratcliffe et al. (2004), Ratcliffe et al. (2006), and Ellwood et al. (2008), a subset of samples were then analyzed using X-ray diffraction (XRD) to determine the whole-rock, > 4 μm and < 4 μm mineralogical composition (Table 2). This approach is adopted here, and was by previous authors,

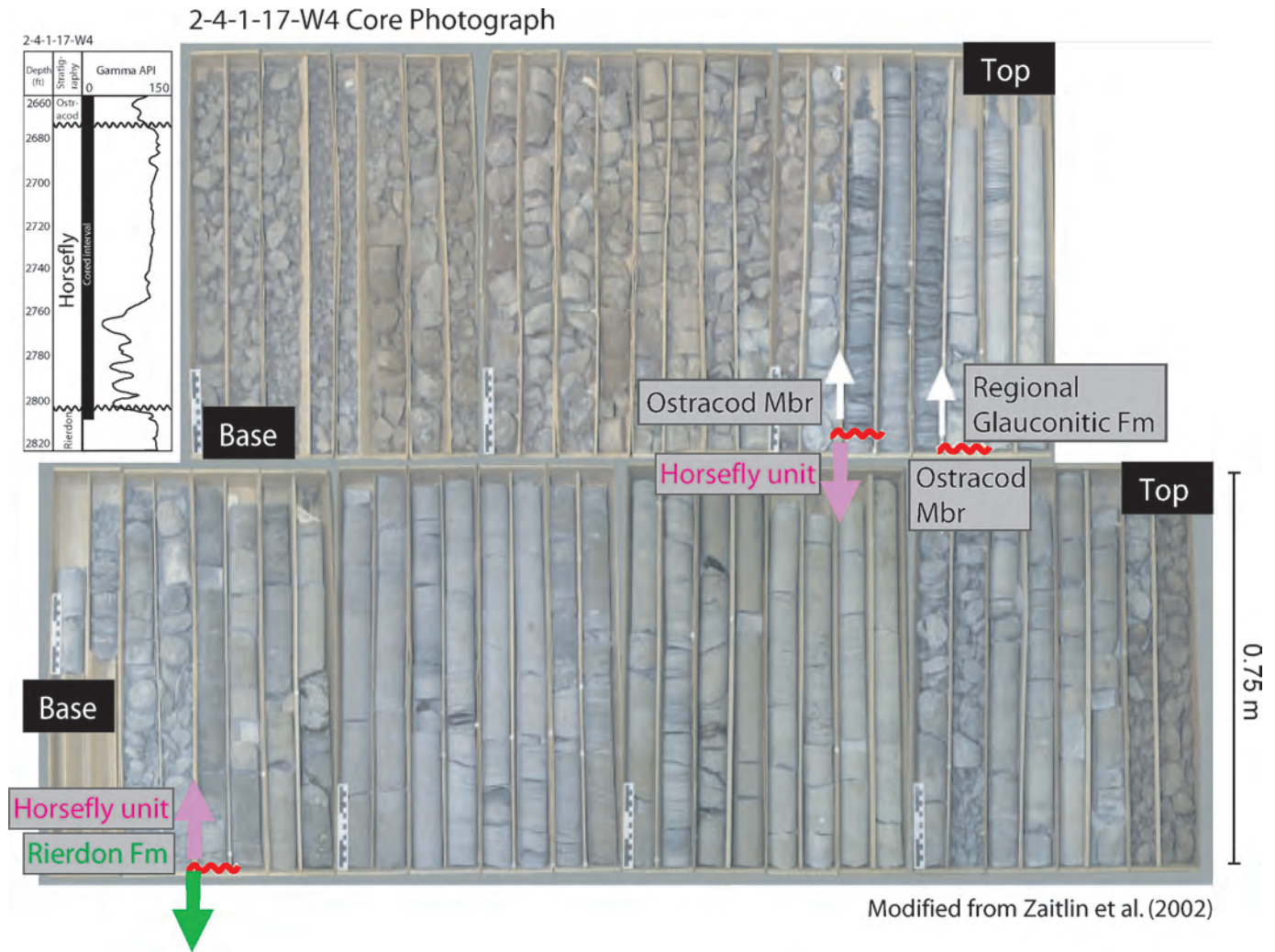


FIG. 4.—Example of typical Horsefly braided-fluvial to coarse-grained meander sandstones, overlain by thick variegated paleosol complex. Modified from figure 18 in Zaitlin et al. (2002).

to help elucidate the mineralogical associations of selected key elements for the chemostratigraphic study.

CHEMOSTRATIGRAPHY OF THE SECOND CYCLE OF THE BASAL QUARTZ

Geochemical Differentiation of Sandstone Lithologies

The cored interval in well 15-32-10-18W4 is interpreted to contain vertically stacked sandstones from the Horsefly, BAT, and Ellerslie units (Figs. 6, 7; Zaitlin et al. 2002). Therefore, well 15-32-10-18W4 is considered to be the informal type section for the second cycle of an upward increase in mineralogical and textural maturity in the Basal Quartz (Zaitlin et al. 2002).

Sandstones of the Horsefly unit in well 15-32-10-18W4 are differentiated from those of the overlying BAT and Ellerslie units by their high K_2O/Al_2O_3 and Rb/Al_2O_3 values (Fig. 7A). Sandstones of the BAT are differentiated from those of the Ellerslie unit by their low Zr/Cr and TiO_2/Al_2O_3 values (Fig. 7A), and sandstones of the Ellerslie unit are differentiated from those of both the Horsefly and BAT units by higher values of Zr/Cr and TiO_2/Al_2O_3 (Fig. 7A). Ratcliffe et al. (2002) and Ratcliffe et al. (2004) demonstrated that the claystone lithologies of the Horsefly, BAT, and Ellerslie units in the Taber–Cutbank Valley are also each geochemically distinctive. Therefore, combining the results here with

the work of Ratcliffe et al. (2002) and Ratcliffe et al. (2004) provides a robust chemostratigraphic characterization of the second cycle of the Basal Quartz in the Taber–Cutbank Valley.

The binary diagrams presented in Figures 7B and 7C show that the geochemistry of sandstones assigned to the Horsefly, BAT, and Ellerslie units are markedly different from one another, as described above from chemical logs. Although the majority of samples assigned to each lithostratigraphic unit plot together in a relatively tight group, there is one sample (1080.0 m from well 15-32-10-W4) assigned to the BAT unit, which plots in association with samples from the Ellerslie unit and one sample assigned to the Ellerslie unit that plots with samples from the BAT unit (1074.5 m from well 15-32-10-W4). This is a common feature of studies using whole-rock geochemistry for stratigraphic characterization, i.e., not all samples from a given population interval lie within a single group on graphical plots (e.g., figs. 6 and 8 in Pearce et al. 2005a; figs. 10 and 11 in Ratcliffe et al. 2007). Typically, these anomalous samples can be regarded as atypical of their parent group. For example, the sample from 1074.5 m in well 15-32-10-18W4 lies in the middle of the Ellerslie unit yet plots in association with samples from the BAT unit. However, the physical position of this sample in the sequence implies that it cannot be part of the BAT unit, despite having Zr/Cr values that are low enough to place it within that unit. Furthermore, the SiO_2 vs. Al_2O_3 binary diagram

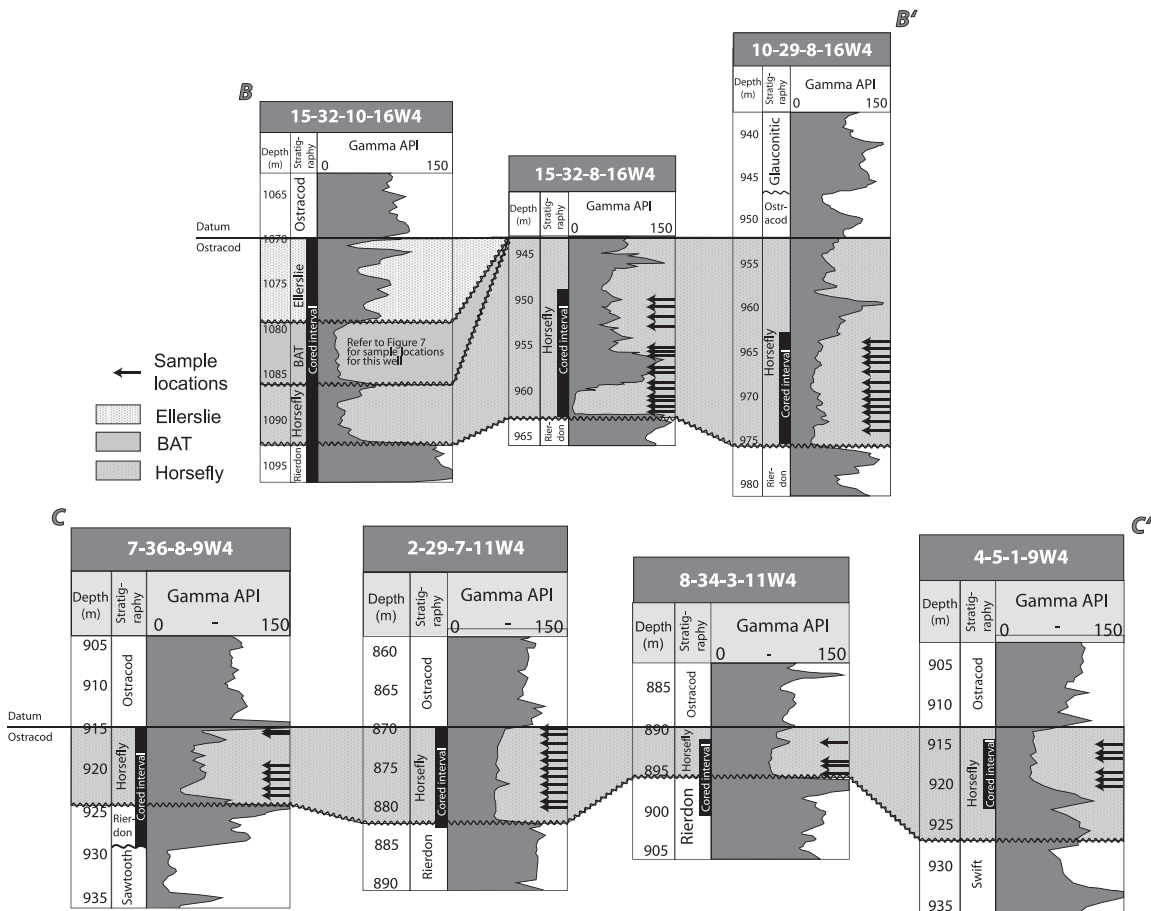
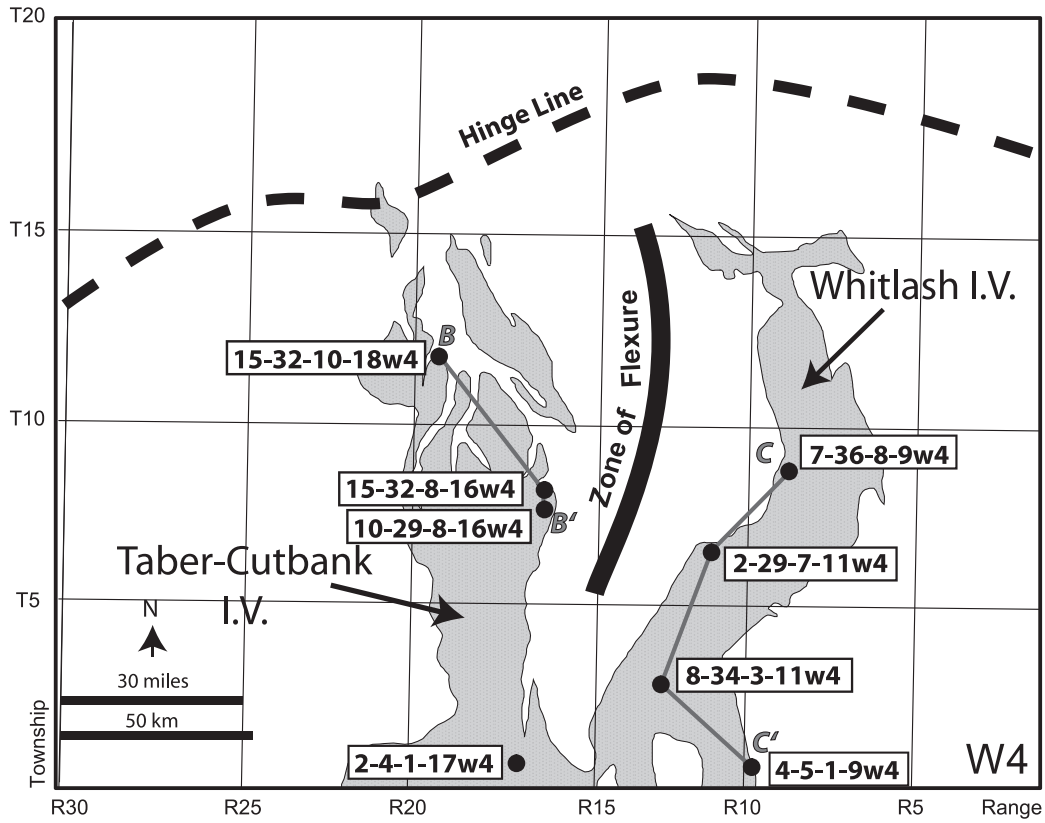


TABLE 1.—Study wells, study intervals, and sample numbers.

Well	Study Interval (m)	Number of core samples			Total sample numbers
		Horsefly	BAT	Ellerslie	
15-32-10-18W4	1071.50–1092.50	12	7	10	29
15-32-8-16W4	950.30–963.30	16	-	-	16
10-29-8-16W4	963.80–974.00	12	-	-	12
7-36-8-9-W4	914.90–925.00	7	-	-	7
2-29-7-11W4	868.60–880.00	12	-	-	12
8-34-3-11W4	892.00–897.50	4	-	-	4
4-5-1-9W4	914.40–918.45	6	-	-	6
TOTAL		69	7	10	86

(Fig. 7D) indicates that the sample from 1074.5 m (well 15-32-10-18W4) is somewhat lithologically anomalous compared to other samples analyzed from this well. The anomalous sample has relatively high Al_2O_3 and low SiO_2 values, indicating that it is more argillaceous than other samples. As discussed below, the mineralogical affinities of Cr are not obvious, but typically it is related to mafic-derived heavy minerals, opaque minerals, or clay minerals (Garver et al. 1996; Singh and Rajamani 2001; Ratcliffe et al. 2007). The linear association of Cr and Al_2O_3 in Figure 7E shows that to some extent Cr is associated with clay minerals in the Basal Quartz. Therefore, the anomalously high Al_2O_3 values in sample 1074.5 m (well 15-32-10-18W4) results in high Cr values and therefore anomalously low Zr/Cr values, i.e. the Zr/Cr values of sample 1074.5 m are anomalous due to it being lithologically different from other samples typical of the BAT unit. Sample 1080.0 m (well 15-32-10-18W4), which is placed in the BAT unit despite its high Zr/Cr values, does not appear to be lithologically anomalous (Fig. 7E), but it does have relatively high Zr values (261 ppm) and low Cr values (10 ppm). No reason for its anomalous Zr and Cr values, relative to other samples of the BAT unit, can be postulated with the current data, but its position in the core, i.e., beneath the top BAT unit unconformity, tends to indicate that a reasonable interpretation based on physical stratigraphic and sedimentological evidence would be to include it in the BAT unit, and it must therefore be considered geochemically anomalous.

When using whole-rock inorganic geochemical data to characterize and correlate sedimentary rocks, it is important to try to understand the controls on the elements and element ratios used to characterize the sediments. The inorganic geochemistry of sediments is influenced by a wide range of geological factors, such as lithological variation, grain size, facies variation, and different diagenetic histories. However, all of these factors change the sediment mineralogy, which is the primary control on sediment geochemistry. As is typical of many chemostratigraphic studies, the elements and element ratios key to understanding the Basal Quartz are relatively few, considering the fifty-element dataset acquired during the analysis. The key elements are Al_2O_3 , K_2O , TiO_2 , Na_2O , Rb, Ga, Zr, and Cr (Figs. 7–9). The general mineralogical controls on these elements have been discussed at length by many authors, including Singh and Rajamani (2001), Armstrong-Altrin et al. (2004), Pearce et al. (2005b), Ratcliffe et al. (2006), Ratcliffe et al. (200), Ratcliffe et al. (2010), Ellwood et al. (2008) and Pe-Piper et al. (2008) and further references cited in those publications. Furthermore, the specific mineralogical controls on the elemental geochemistry of the Basal Quartz have been discussed at length by Ratcliffe et al. (2002); Ratcliffe et al. (2004) and Wright et al. (2010), where geochemical data from the Lower Mannville Formation are

integrated with XRD and heavy-mineral data to provide a clear understanding of the mineralogical controls on the whole-rock geochemistry. The work of those authors is largely used to make the following interpretations, together with the extensive petrographic work on the Basal Quartz previously presented in Zaitlin et al. (2002).

K_2O , Na_2O , Al_2O_3 , Rb, and Ga all occur in clay minerals and feldspars. Variations in their ratios are likely reflecting changes in the amounts and types of these minerals. The high $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ values that typify the Horsefly unit (Fig. 7) were demonstrated by Ratcliffe et al. (2004) to be reflective of the high illite:kaolinite ratio of this unit compared to that of the BAT and Ellerslie units. This interpretation is supported by the low Ga/Rb values of the Horsefly unit (Fig. 7), since Ga/Rb has been shown to reflect kaolinite abundances in fluvial settings (Ratcliffe et al. 2010). A distinguishing petrographic feature of the Horsefly unit compared to the BAT and Ellerslie unit is the presence of minor amounts of K-feldspar (Zaitlin et al. 2002), which could also increase the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ values in the Horsefly unit relative to the younger units. The XRD data in Table 2 do not record K-feldspar, but this could reflect the far smaller dataset here compared to that of Zaitlin et al. (2002).

Na_2O typically occurs in clay minerals, plagioclase feldspar, and evaporites. No evaporites are recorded from the Basal Quartz, and therefore Na_2O is likely controlled by changes in clay mineralogy or in variations in plagioclase feldspar contents. The XRD data in Table 2 indicate that plagioclase is slightly more prevalent in the Horsefly unit of the Whitlash Valley, which is coincident with higher Na_2O values, implying that the Na_2O in the Basal Quartz is to some extent reflecting abundance of plagioclase feldspar.

Zr, Cr, and TiO_2 in sandstones are all elements linked to a large extent to heavy minerals (Armstrong-Altrin et al. 2004; Pearce et al. 2005a; Pe-Piper et al. 2008). Therefore, the changes in whole-rock geochemistry of the sandstone lithologies at the BAT unit/Ellerslie unit unconformity are probably related to changes in sedimentary provenance. This hypothesis is supported by the work of Ratcliffe et al. (2004), who demonstrated that in the Basal Quartz, Zr is related to zircon, Cr to Cr-spinel, and TiO_2 to rutile and that changes in the heavy-mineral indices (*sensu* Morton and Hallsworth 1994) indicate changing sediment provenances during deposition of the Basal Quartz.

Longitudinal Variation of the Horsefly Unit in the Taber–Cutbank Valley

In order to assess whether longitudinal variability in the whole-rock geochemistry in the Taber–Cutbank Valley is greater than the temporal variation throughout the Basal Quartz, samples from the Horsefly unit

FIG. 5.—Schematic map showing the approximate extent of the Horsefly in southern Alberta and the location of wells that form this study. Redrawn from Zaitlin et al. (2002). I.V. = Incised Valley. B–B' and C–C' refer to correlation panels constructed for study wells in the Taber–Cutbank Valley and the Whitlash Valley, respectively. The black arrows against the gamma-ray log represent the locations of the sandstone core samples analyzed.

TABLE 2.—Results from X-ray diffraction analyses. TCIV = Taber-Cutbank Incised Valley; WIV = Whitlash Incised Valley. Chl = chlorite, Kaol = kaolinite, Ill/Mica = illite mica, Mix IS = mixed-layer illite-smectite, Cal = calcite, Dol = dolomite, Sider = siderite, Qtz = quartz, K-spar = potassium feldspar, Plag = plagioclase feldspar, Carb = Carbonates.

Sample Detail			CLAYS				CARBONATES			OTHER MINERALS				TOTALS		
Valley	Well	Depth (m)	Chl	Kaol	Ill/Mica	Mx IS	Cal	Dol	Sider	Qtz	K-spar	Plag	Pyrite	Clays	Carb.	Other
TCIV	10-29-8-16W4	968.3	0	2	1	Tr	0	0	0	96	0	0	1	3	0	97
TCIV	10-29-8-16W4	971.6	0	2	1	Tr	0	0	0	96	0	0	1	3	0	97
TCIV	15-32-8-16W4	956.2	0	5	2	0	0	0	0	93	0	0	Tr	7	0	93
TCIV	15-32-8-16W4	961.9	0	2	1	Tr	Tr	Tr	0	97	0	0	Tr	3	Tr	97
WIV	4-5-1-9W4	1218.4	0	4	0	Tr	Tr	Tr	Tr	96	0	Tr	Tr	4	Tr	96
WIV	4-5-1-9W4	920.2	0	4	1	Tr	0	0	11	84	0	Tr	Tr	5	11	84
WIV	2-29-7-11W4	874	0	6	Tr	0	0	0	0	94	0	2	Tr	6	0	94
WIV	2-29-7-11W4	878	0	6	Tr	0	0	0	Tr	94	0	Tr	0	6	Tr	94

were analyzed from wells 10-29-8-16W4 and 15-32-8-16W4. These wells lie approximately 10 km to the south of well 15-32-10-18W4 in the Taber-Cutbank Valley (Fig. 5). Figure 8 shows the Horsefly unit samples from wells 10-29-8-16W4 and 15-32-8-16W4, together with the Horsefly unit samples from the type well, 15-32-10-18W4. The samples are plotted on a binary diagram with the same axes as those used to differentiate the Horsefly, BAT, and Ellerslie units in the type well (Fig. 7B, C). All of the samples from wells 10-29-8-16W4 and 15-32-8-16W4 clearly plot in the field defined by the Horsefly unit samples from well 15-32-10-18W4. This demonstrates that longitudinal changes in whole-rock geochemistry in the

Horsefly unit along this reach of the Taber-Cutbank Valley are minor when compared to the changes vertically between stratigraphic units (i.e., BAT and Ellerslie units).

Geochemistry of the Horsefly Unit in the Taber-Cutbank and the Whitlash Valleys

The Horsefly unit, as discussed in the “Regional Background” section, occurs in both the western Taber-Cutbank Valley and the eastern Whitlash Valley (Figs. 1, 5; Zaitlin et al. 2002), i.e., the Basal Quartz

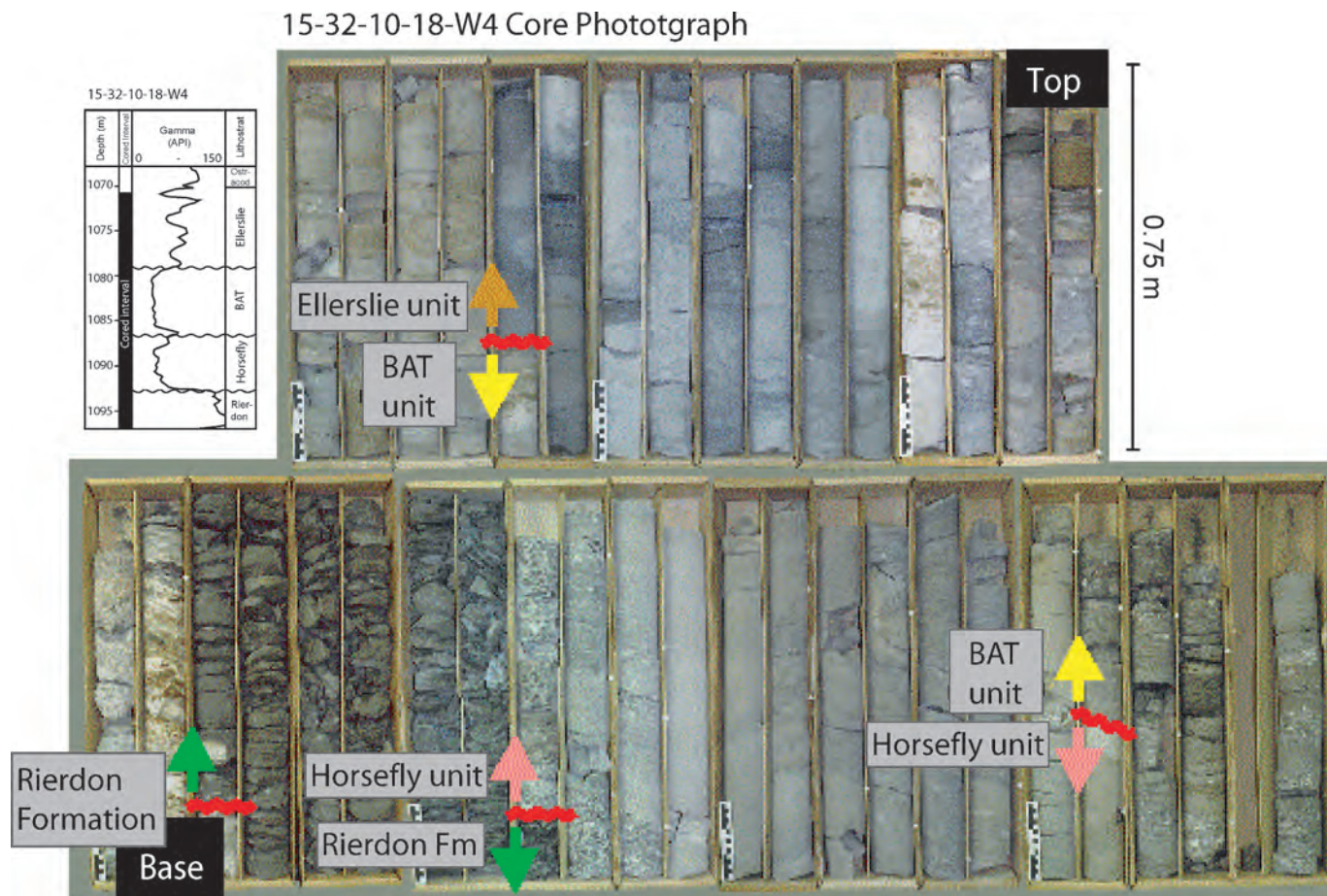
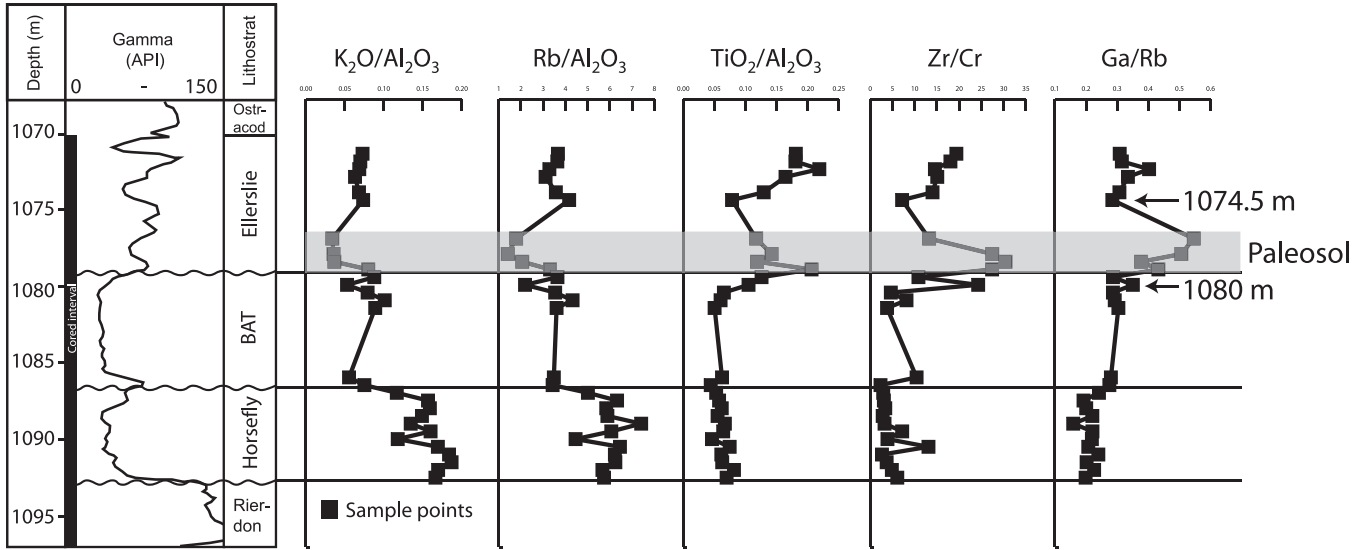
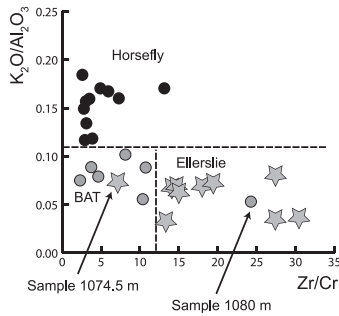


FIG. 6.—Core photograph; well 15-32-10-18W4. Basal unconformities of each of the Horsefly, BAT, and Ellerslie units are marked as wavy lines and can be directly compared to the position of these unconformities marked on the gamma log.

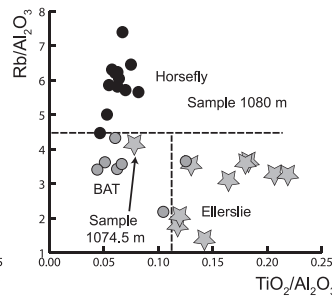
A) 15-32-10-18-W4 (type section)



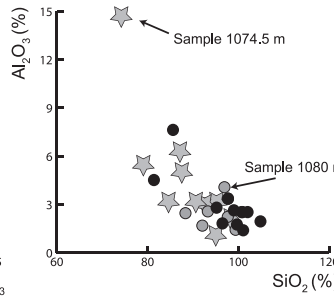
B) 15-32-10-18-W4 (type section)



C) 15-32-10-18-W4 (type section)



D) 15-32-10-18-W4 (type section)



E) 15-32-10-18-W4 (type section)

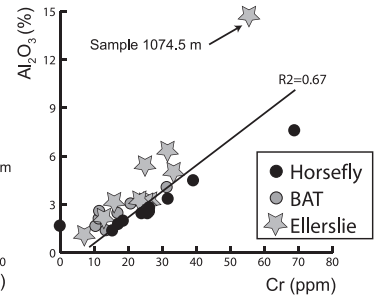


Fig. 7.—Characterization of Horsefly, BAT, and ELLERSLIE sandstones in well 15-32-10-18-W4 (Taber–Cutbank Valley) using A) chemical logs and B, C) binary diagrams. Each black square in 5A represents an analyzed sandstone core chip. Parts B and C demonstrate the differentiation of the three units in well 15-32-10-18-W4 using binary diagrams. Part D highlights the high Al₂O₃ and low SiO₂ concentrations in sample at 1074.5m in well 15-32-18-W4. Part E demonstrates that Cr has a positive linear relation with Al₂O₃.

sediments in the Whitlash Valley are lithostratigraphically similar to the Horsefly unit of the Taber–Cutbank Valley. In active tectonic areas, like the WCSB in the Early Cretaceous, variations in basin geometry and source area promote variations in sediment composition between incised-valley systems. Figure 9A and B show that largely sandstone samples of the Horsefly unit in the Whitlash Valley plot in clusters that are different from either the BAT or ELLERSLIE units in well 15-32-10-18-W4 (Taber–Cutbank Valley); thereby the weight of data supports the interpretation of Zaitlin et al. (2002) that the Basal Quartz sandstones in the Whitlash Valley belong to the Horsefly unit. However, the separation of samples clusters in Figure 9A and B is not as well defined as in Figure 9C–F, with several of the Whitlash Valley Horsefly unit samples plotting in association with both the BAT and ELLERSLIE unit samples of the Taber–Cutbank Valley. This overlap is most probably due to anomalous samples, which, as discussed above, commonly occur in chemostratigraphic studies. Potentially, however, the overlapping samples could imply that the Horsefly unit of the Whitlash Valley has some influence from the BAT and ELLERSLIE units of the Taber–Cutbank Valley, resulting in reworking of the Horsefly unit in the Whitlash Valley and incorporation of these sediments into BAT and ELLERSLIE sediments. This hypothesis cannot be tested with the current dataset, but it could be tested by analysis of more wells from the south of the current study area in

northern Montana, where the Taber–Cutbank and Whitlash valleys appear to amalgamate (Fig. 5).

Despite Zaitlin et al. (2002) demonstrating that the Basal Quartz sediments in the Whitlash Valley are stratigraphically interpreted as the Horsefly unit, Figure 9C–F demonstrate that the whole-rock geochemistry of Horsefly unit sandstones in the Taber–Cutbank Valley is markedly different from that of the Horsefly unit sandstones in the Whitlash Valley. The Horsefly unit sandstones deposited in the Whitlash Valley are generally enriched in Al₂O₃ and Na₂O (Fig. 9C, D). Furthermore, they have low K₂O/Al₂O₃ values and high Cr/Al₂O₃ values compared to the sandstones of the Horsefly unit in the Taber–Cutbank Valley (Fig. 9E, F). Therefore, although the Horsefly unit is the same gross lithostratigraphic unit in the Taber–Cutbank and Whitlash valleys it is considered a separate chemostratigraphic unit in each valley. The lateral variation in whole-rock geochemistry between valley systems appears to be greater than the temporal variations described within the Basal Quartz of the Taber–Cutbank Valley.

DISCUSSION

The premise of using chemostratigraphy as a tool for stratigraphic correlation is based on using changes in whole-rock geochemistry as

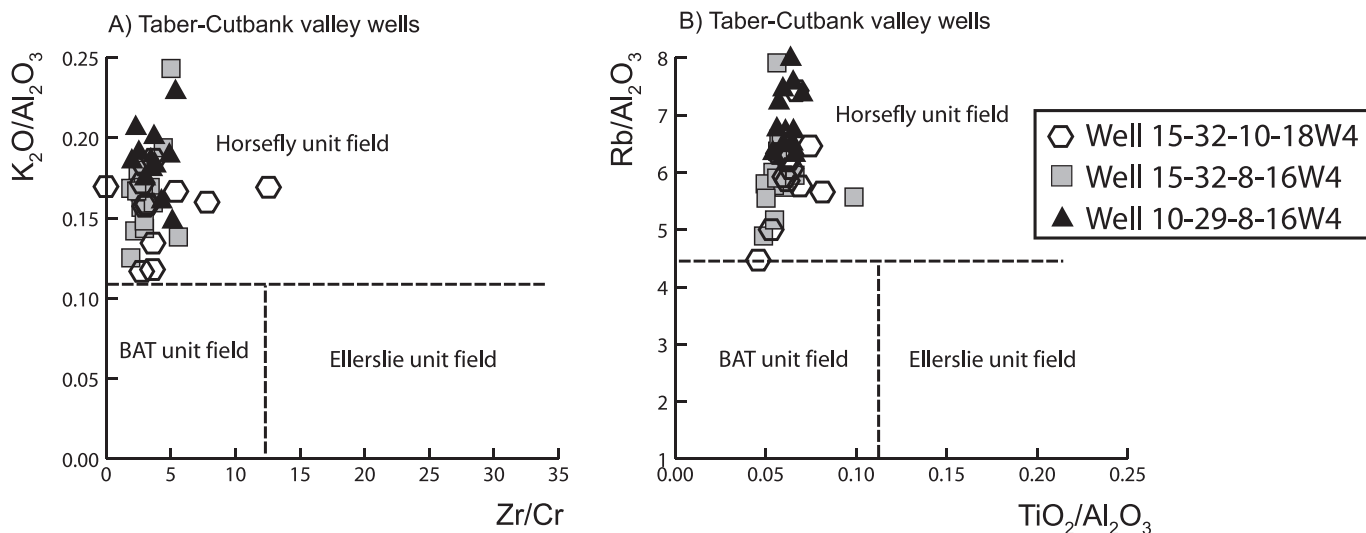


Fig. 8.—Horsefly unit samples from wells 15-32-10-18W4, 15-32-8-16W4, and 10-29-8-16W4 (see Fig. 5 for well locations) plotted on binary diagram templates used in Figure 7 to characterize the three units of the second cycle in the Basal Quartz.

proxies for provenance changes (Pearce et al. 2005b; Ratcliffe et al. 2010; Wright et al. 2010), paleoclimate changes (Ratcliffe et al. 2010), changes in paleo-redox conditions (Tribouillard et al. 2006), or other features in the sediments that have potential to enable stratigraphic correlation. The assumption is that in a given area, approximately coeval homotaxial units retain a geochemical signature over longitudinal distances sufficient to allow the geochemical changes that occurred through time to be used to build a chemostratigraphic framework. In moderate- to high accommodation fluvial settings, this approach has been demonstrated to be successful in the Carboniferous Barren Red Measures of the Southern North Sea (Pearce et al. 2005a; Pearce et al. 2005b), the Triassic TAG-I of Algeria (Ratcliffe et al. 2006), and the Triassic Mungaroo Formation on the North West Shelf of Australia (Ratcliffe et al. 2010). However, due to the polyphase erosion and deposition characteristic in low-accommodation compound incised-valley settings and the long time periods represented by thin, preserved sedimentary sequences, the potential for coeval homotaxial deposits in adjacent compound incised-valley systems to have markedly different whole-rock geochemical signatures is increased. Additionally, in active tectonic areas, like the WCSB in the Early Cretaceous, variations in basin geometry and changes in the sediment source areas are more likely to result in variations in sediment composition between incised-valley systems. The results presented here demonstrate that chemostratigraphy is an effective stratigraphic tool in low-accommodation settings and can also potentially aid in understanding and refining detailed stratigraphic relationships between homotaxial units.

The sandstones of each of the three component units of the second cycle of the Basal Quartz have distinctive inorganic whole-rock geochemical signatures (Fig. 7). Ratcliffe et al. (2002) and Ratcliffe et al. (2004) demonstrate that the claystone lithologies of these three units are also geochemically distinctive. By combining the work presented here for sandstones from the Taber–Cutbank Valley with the work of Ratcliffe et al. (2002) and Ratcliffe et al. (2004) from the same valley system, it is apparent that the Horsefly, BAT, and Ellerslie lithostratigraphic units defined by Zaitlin et al. (2002) are *chemostratigraphic units* in the Taber–Cutbank incised-valley system. Longitudinally in the Taber–Cutbank Valley, the Horsefly unit shows no significant changes in the key element ratios that were used to differentiate the Horsefly, the BAT, and the Ellerslie units in the type well (15-32-10-18W4) (Figs. 6, 7), i.e., in the Taber–Cutbank valley longitudinal changes in geochemistry are less

significant than the changes in elemental compositions that took place through time during deposition of the Basal Quartz. However, the geochemical signature of the Horsefly unit in the Taber–Cutbank Valley is different from that for the same lithostratigraphic unit in the Whitlash Valley (Fig. 9), i.e., the variation within the Horsefly unit between valley systems is greater than the geochemical changes that took place during deposition of the Basal Quartz. As a result of the differing geochemistries of the Horsefly unit between the two valley systems, incorrect stratigraphic conclusions would have been drawn if chemostratigraphy had been used in isolation from other datasets; the Lower Mannville Formation sandstones in the Whitlash Valley would have been classified as a stratigraphic unit separate from any of those of the Basal Quartz in the Taber–Cutbank Valley. Because the Horsefly unit is known to be homotaxial between the two valley systems (Zaitlin et al. 2002), however, the chemostratigraphic data indicate that the Horsefly unit must comprise two sub units, one in the Taber–Cutbank Valley and one in the Whitlash Valley. By consideration of the geochemical differences between the two subunits, a better understanding of the stratigraphic relationships in the two valleys can be gained.

Although the potential influences on whole-rock geochemistry are numerous, such as lithological changes, grain-size variation, sedimentary facies, paleoclimate, provenance, and/or diagenesis, the control on elemental composition of sediments is based on mineralogy. By understanding the mineralogical controls on elements used to characterize sediments, inferences can then be made about changes in paleoclimate, facies, provenance, and diagenesis.

The Horsefly subunit of the Whitlash Valley has high Al_2O_3 and low K_2O relative to the Horsefly subunit of the Taber–Cutbank Valley (Fig. 9A, C). With the absence or low abundance of K-feldspar from most samples (Table 2), the most likely controls on the distribution of K_2O and Al_2O_3 will be changes in the clay mineralogy. Kaolinite, $Al_4(Si_4O_{10})(OH)$ is more aluminous relative to illite, $K_{1-1.5}Al_4(Si_{7-6.5}Al_{1-1.5}O_{20})(OH)_4$, (including illite–smectite and illite mica), and the XRD data indicate that the sandstones of the Whitlash Valley are relatively kaolinitic compared to those of the Taber–Cutbank Valley (Table 2). Therefore, the lowered K_2O/Al_2O_3 values of the Whitlash Valley sandstones are likely due to high kaolinite content. The change in kaolinite content between the two valleys (Table 2) suggests that the sandstones of the Whitlash Valley have been subjected to a greater degree of weathering. Measured east to west from the valley edges at Township 10, the two

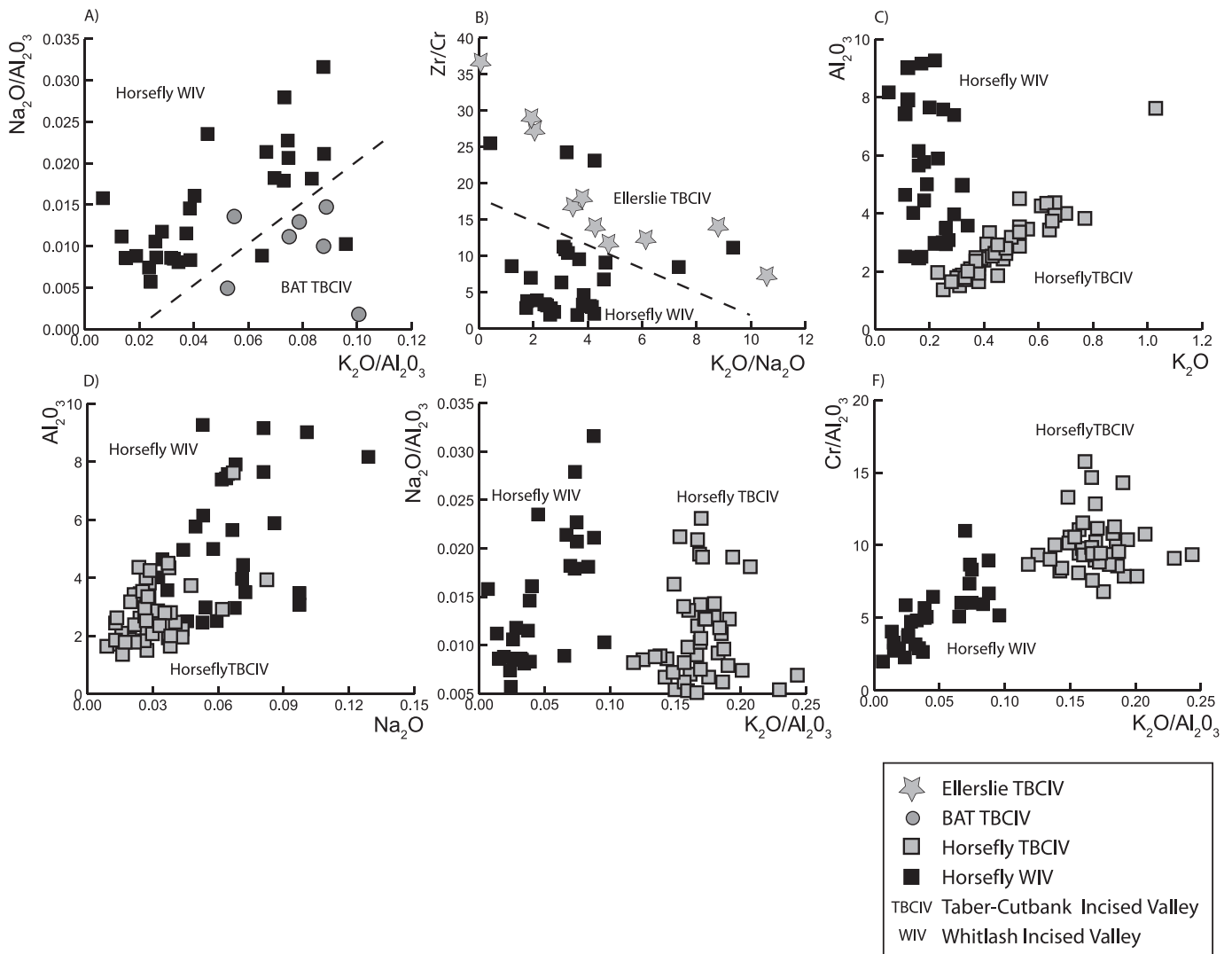


FIG. 9.—Comparison of sandstone whole-rock geochemistry of the Basal Quartz in the Taber–Cutbank Valley and the Whitlash Valley. Parts A and B demonstrate that apart from a small number of samples, all Horsefly unit samples analyzed from the Whitlash Valley are chemically different from those of the BAT and Ellerslie units, respectively. Parts C–F highlights the geochemical differences in the Horsefly unit between the two valleys.

valley systems are approximately 40 miles (65 km) apart (Fig. 5) and there is no evidence of any feature that could result in differing microclimates. Therefore, it is suggested here that the increase in sediment weathering may reflect an increased surface residence time for the Whitlash Valley Horsefly subunit relative to that of the Taber–Cutbank Valley Horsefly subunit. This is supported by the work of Zaitlin et al. (2002), who calculated that sedimentation rates in the area of the Whitlash Valley were less than 2.2 m/Myr whereas sedimentation rates in the Taber–Cutbank Valley were as high as 6.6 m/Myr. Furthermore, the same authors demonstrated that the area of the Whitlash Valley during deposition of the Basal Quartz was characterized by long periods of erosion and exposure, and development of mature paleosols.

Figure 9B demonstrates that the sandstones from the Whitlash Valley have higher Na₂O values than those from the Taber–Cutbank Valley. This potentially reflects the minor amounts of plagioclase feldspar in the sandstones of the Whitlash Valley and the absence of this mineral phase from the sandstones of the Taber–Cutbank Valley (Table 2). Figure 9D shows that the sandstones of the Whitlash Valley have lower Cr/Al₂O₃

values than those of the Taber–Cutbank Valley. The mineralogical affinities of Cr are not readily obvious in this dataset, but in siltstones and sandstones this element is commonly associated with mafic-derived heavy minerals, opaque minerals, or clay minerals (Garver et al. 1996; Singh and Rajamani 2001; Ratcliffe et al. 2007). The changes in both Na₂O values and Cr/Al₂O₃ values suggest a change in detrital mineralogy that is best explained by the two valley systems having a different sediment provenance during deposition of the Horsefly unit. The Whitlash Valley provenance was rich in plagioclase and poor in mafic material relative to the provenance of the Taber–Cutbank Valley. In the past, the Horsefly unit in the Whitlash and Taber–Cutbank valleys has been interpreted as coeval and the product of two northward-flowing channels, separated by an interfluvial area, which is likely to represent the position of the peripheral forebulge during this time period of the WCSB (Zaitlin et al. 2002). This situation cannot fully explain the different sediment provenances of the Horsefly unit in the two valley systems. An alternative interpretation is that the Whitlash Valley could be a southward-flowing tributary of the northward-flowing Taber–Cutbank Valley system, with a confluence south of Range 15 on the USA–Canada border (Fig. 5). As

discussed above, this would potentially explain the overlap of samples in Figure 9A and B. This hypothesis could be tested by expanding the study area into northern Montana, but that was beyond the scope of this study.

A simpler explanation would be that the Horsefly unit in the Taber–Cutbank is not coeval with the Horsefly unit in the Whitlash Valley, despite being homotaxial, and that the Horsefly unit comprises two, noncoeval subunits, one that is present in the Taber–Cutbank Valley and one that is present in the Whitlash Valley. With the current dataset, this latter hypothesis is favored.

CONCLUSIONS

Chemostratigraphy is a viable correlation tool for the development or calibration of pre-existing stratigraphic frameworks in low-accommodation settings. However, its application in such settings requires a working understanding of the regional geology, an appreciation of the sequence stratigraphy, and input of mineralogical data. By carefully integrating whole-rock geochemistry with these other datasets, the technique not only is a valid correlation tool, but it also potentially refines pre-existing stratigraphy and adds to the understanding of basin evolution.

Changes in key elements and element ratios are used to differentiate the Horsefly, BAT, and Ellerslie units within a single compound incised valley, the Taber–Cutbank Valley. These changes are of greater magnitude than longitudinal changes in the same ratios within a single unit, the Horsefly unit, i.e., the longitudinal changes in geochemistry do not preclude units of different ages being chemostratigraphically defined within a single valley system.

There are marked differences between the whole-rock geochemistry of one homotaxial lithostratigraphic unit, the Horsefly unit, between the Taber–Cutbank Valley and the Whitlash Valley. As a result, if chemostratigraphy had been carried out on the dataset acquired for this paper in isolation, the Horsefly unit in the Whitlash Valley would have been incorrectly stratigraphically assigned. However, by utilizing the chemostratigraphic results in a regional stratigraphic context, it is shown that the Horsefly unit is in fact two subunits, one that occurs in the Taber–Cutbank Valley and one that occurs in the Whitlash Valley and that the two subunits are homotaxial, but not coeval. Therefore, the previous interpretation that the Horsefly unit was synchronously deposited in two northward-flowing distributaries is demonstrated to be incorrect.

The compound incised valleys of the Lower Mannville Formation are in many ways typical of low-accommodation settings around the world, and the methods employed here in using whole-rock geochemical data to understand stratigraphy and basin development are applicable to any other (economically) important sequences deposited in low-accommodation fluvial incised-valley settings.

Ongoing chemostratigraphic work extending the stratigraphic study interval (see Wright et al. 2010 for Upper Mannville and Basal Colorado extension) and the geographic coverage is currently underway with the aim of creating a chemostratigraphic scheme of the Jurassic–Cretaceous sequences of the WCSB that can be used in conjunction with existing lithostratigraphic, chronostratigraphic, and sequence stratigraphic schemes.

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