Chemostratigraphic Methodologies

THE APPLICATION OF CHEMOSTRATIGRAPHIC TECHNIQUES TO DISTINGUISH COMPOUND INCISED VALLEYS IN LOW-ACCOMMODATION INCISED-VALLEY SYSTEMS IN A FORELAND-BASIN SETTING: AN EXAMPLE FROM THE LOWER CRETACEOUS MANNVILLE GROUP AND BASAL COLORADO SANDSTONE (COLORADO GROUP), WESTERN CANADIAN SEDIMENTARY BASIN

AMELIA M. WRIGHT AND KENNETH T. RATCLIFFE
Chemostrat Inc., 5850 San Felipe, Suite 500, Houston, Texas 77057, U.S.A.
e-mail: millywright@chemostrat.co.uk; kenratcliffe@chemostrat.co.uk
BRIAN A. ZAITLIN
Enerplus Resources, 333-7th Avenue S.W, Suite 3000 Calgary, Alberta T2P 2Z1, Canada
e-mail: bzaitlin@enerplus.com
AND
DAVID S. WRAY
University of Greenwich, Grenville Building, Pembroke (area), Chatham Maritime, Kent, ME4 4TB U.K.
e-mail: d.wray@greenwich.ac.uk

ABSTRACT: Changes in the bulk inorganic geochemical composition of both sandstones and silty mudstones taken from conventional cores are used to subdivide the Lower Cretaceous Mannville Group and the overlying Colorado Group into chemostratigraphic packages and geochemical units. The chemostratigraphic packages are broadly equivalent to lithostratigraphic formations whereas the geochemical units are represent finer-scale informal stratigraphic subdivisions that occur within the formations.

The chemostratigraphic packages are equivalent to the Lower Mannville Formation, the Upper Mannville Formation, the Basal Colorado Sandstone (an informal unit at the base of the Colorado Group), and the overlying Joli Fou Formation. The changes, which enable each lithostratigraphic unit, or chemostratigraphic package, to be geochemically fingerprinted, are primarily related to changes in mineralogy, which in turn appear to coincide with changes in sediment provenance and basin architecture. These chemostratigraphic packages, which are broadly equivalent to lithostratigraphic formations, can be considered to result from first-order changes in whole-rock geochemistry.

The geochemical units are equivalent to incised-valley-fill sequences within the lithostratigraphic units, and here it is shown that the incised-valley-fill sequences of the Upper Mannville and Basal Colorado Sandstone each have a unique geochemical signature. Three incised-valley-fill sequences are present in the latter intervals, the oldest of which lie within the Upper Mannville Formation. Valleys at the base of the Basal Colorado Sandstone incise Upper Mannville deposits and are termed the lower Basal Colorado sandstones. The youngest valleys lie at the top of the Basal Colorado Sandstone and are termed the upper Basal Colorado sandstones. The sedimentary deposits in each of these incised valleys can be chemically distinguished from one another, even where a sandstone-on-sandstone contact is present in a single wellbore. The geochemical changes that enable each incised-valley fill to be recognized can be considered as second-order variations and are referred to as geochemical units. Stacked valleys observed in the Lower Mannville Formation have been the subject of previous chemostratigraphic work, and all of these have a unique geochemical signature and are also considered here to be geochemical units.

The base of each incised-valley-fill succession, or geochemical unit, is a sequence boundary. By enabling clear identification of the geochemical unit above and below a sequence boundary, the technique of chemostratigraphy has direct application to aiding both lithostratigraphic and sequence stratigraphic correlations in low-accommodation basin settings.

KEY WORDS: chemostratigraphy, incised valleys, Mannville Group, Colorado Group

INTRODUCTION

Subdivision of sedimentary sequences in low-accommodation, fluvially dominated depositional environments is at times problematic, due to their complex stratigraphy (e.g., Zaitlin et al., 1994; Zaitlin et al., 2002; Boyd et al., 2006). The complexity arises from a lack of well preserved fauna and flora, lack of discernible widespread continuous markers, and juxtaposition of sandstone of differing ages by polyphase incision and development of homotaxial units (Zaitlin et al., 2002). These difficulties are further compounded when dealing with subsurface data, as in the case of most petroleum basins, due to the essentially one-dimen-

sional nature of data offered by well bores (Cant, 2005). Some of the most difficult sedimentary sequences to differentiate occur in low-accommodation fluvial settings in which multiple incisions prevent differentiation of incised-valley-fill deposits that are of a different age, irrespective of the depth to which they incise.

The Mannville Group and Basal Colorado Sandstone of the overlying Colorado Group of southern Alberta comprise fluvial and shoreface sandstones and silty mudstones deposited in a low-accommodation, foreland-basin setting. Compound incised-valley systems form the majority of the units and are produced by the multicyclical falls and rises of base level. The Basal Colorado Sandstones, which form an informal unit comprising the oldest

Colorado Group sediments in the study area, are overlain by the marine mudstones of the Joli Fou Formation, which marks a major marine transgression in the area. Details of the depositional settings and stratigraphy of the Lower Mannville Formation are found in Leckie et al. (1994).

The interval encompassed by the Lower Cretaceous Mannville Group to Basal Colorado Sandstone is a much studied one, largely due to the exploration for and exploitation of hydrocarbons. The sequence is one of the most prolific hydrocarbon-bearing successions in the Western Canada Sedimentary Basin (WCSB), with hydrocarbons being produced from the Lower Mannville Formation, the Upper Mannville Formation, and the Basal Colorado Sandstone. Reservoirs of the Upper Mannville Formation (Fig. 1) are productive from the Glauconitic through Colony sands. In southern Alberta, shoreface and incised-valley-fill sequences form the large pools. Smaller pools within this play are a result of stratigraphic traps or small structural features. The play was first discovered in 1917, and since then in excess of 13,496 pools have been found, containing 33.9 Tcf original gas in place. Basal Colorado Sandstone reservoirs were first discovered in 1940, and by 2006, 249 pools were found. The discovered pools contain 1.6 Tcf original gas in place, although the play is dominated by one significant pool, the Cessford Basal Colorado A pool at 738 Bcf original gas in place. The reservoirs occur in three broad facies: fluvial channels incised into the Mannville Group, shore-parallel, fining-upward, trough cross-stratified pebbly sandstones, and northwest–southeast trending transgressive shorefaces.

The Mannville Group is divisible into the Lower Mannville Formation, composed of the Basal Quartz (BQ) and the overlying Ostracod Member, and the Upper Mannville Formation, comprising the succession which includes the Glauconitic Formation and undifferentiated nonmarine mudstones and sandstones. The top of the Mannville Group is marked by the Basal Colorado Sandstone, which is an informal unit at the base of the Colorado Group (Fig. 1). The Mannville Group comprises northward-prograding fluvial and shoreface sediments (Wightman, 1982; Hayes et al., 1994; Wood, 1996) sourced from the south. These sediments are unconformably overlain by fluvially incised valley fills and shoreface deposits of the Basal Colorado Sandstone. The sandstones that constitute the Basal Colorado Sandstone were sourced from the east; the sedimentary units prograded approximately westward. Within the Basal Colorado Sandstone, two petrographically distinctive valley-fill sandstones have been recognized, a smectite-rich lithic sandstone and a quartz-rich sandstone, the latter being associated with upper Basal Colorado sandstones (Walker, 2002). The top surface of the Upper Mannville Formation is described by Walker (2002) as a flooding-surface sequence boundary (FSSB) where it is overlain by Basal Colorado Sandstone shoreface deposits, which resulted from a fall and rise in relative sea level. During the fall in sea level, valleys were incised into the Upper Mannville Formation. These valleys were filled during the subsequent sea-level rise, and the resultant valley-fill sandstones are termed the lower Basal Colorado sandstones. Continued sea-level rise allowed a series of shoreface deposits to onlap the top surface of the lower Basal Colorado Sandstones. These shoreface deposits, termed the Basal Colorado sandstones, consist of an assemblage of shallow marine fining-upward successions of trough cross-stratified conglomerates, sandstones, and mudstones containing a mixed restricted *Skolithos–Cruziana* ichnofacies assemblage (Leroux and MacEachern, 2000). Following the transgression and deposition of the Basal Colorado Sandstone shoreface deposits, a second fall and rise in base level resulted in the top Basal Colorado FSSB (Walker, 2002) (Fig. 2). The upper Basal

Colorado Sandstone sediments are quartz-rich and fill the incised valleys that resulted from the base-level fall. Following deposition of the Basal Colorado Sandstone, a major reorganization of the basin occurred, and the Joli Fou Formation prograds from east to west (Fig. 2).

Therefore, in southern Alberta, within the sequences that encompass the Mannville Group and Basal Colorado Sandstone, there are multiple potential incised-valley-fill systems, all of which are superficially similar to one another in terms of lithology and distribution. Furthermore, due to the low-accommodation setting these superficially similar incised-valley-fill sediments can incise into one another. Well 15-32-10-18W4 reported by Hildred et al. (2008) is an example in which three incised-valley-fill sandstones of the Lower Mannville Formation are erosionally juxtaposed on top of one another. Such situations, where two or more sandstones are in direct contact in a single well bore, can provide invaluable insight to the stratigraphy of a basin, provided that the sandstones can be clearly assigned to a specific valley fill.

Previous whole-rock chemostratigraphic studies on fine-grained facies in the Lower Mannville Formation (Ratcliffe et al., 2002; Ratcliffe et al., 2004; Hildred et al., 2007, 2008) distinguished three incised-valley systems of differing ages, which are coincident with the Horsefly, Bantry-Anderson Taber (BAT), and Ellerslie lithostratigraphic units (Zaitlin et al., 2002). The works of Ratcliffe et al. (2002) and Ratcliffe et al. (2004) published only data acquired from the fine-grained facies of the Lower Mannville Formation to demonstrate this chemostratigraphic characterization. Hildred et al. (2007, 2008) demonstrated that the sandstones from each of the three units are geochemically distinctive. The work of those authors concentrated on a valley fill of the Horsefly unit in the Lower Mannville Formation. The Horsefly unit was shown to be deposited in two subparallel valley systems (Zaitlin et al., 2002), and Hildred et al. (2008) demonstrated that the geochemistry of the Horsefly unit varies markedly between the two valley systems.

Here an approach to chemostratigraphy similar to that of Hildred et al. (2007, 2008) is adopted, but instead of determining lateral variations in geochemistry between two coeval valley systems, stacked units of differing ages are distinguished using data acquired from both sandstone and mudstone lithologies. The broadening of the work to include both sandstone and mudstone lithologies is an important extension, since fine-grained facies in low-accommodation fluvial settings are often volumetrically less than the sandstone lithologies. Furthermore, by combining data acquired for this paper from the Upper Mannville Formation, the Basal Colorado Sandstone, and the Joli Fou Formation with data acquired by previous authors (Ratcliffe et al., 2004, Hildred et al., 2007, 2008) from the Lower Mannville Formation, the geochemical data acquired characterizes incised-valley-fill sediments that cover a longer time span than existing studies in the Western Canadian Sedimentary Basin. Expanding the chemostratigraphic analysis of the interval is an important aspect of this study, since chemostratigraphy is generally used on restricted stratigraphic intervals (Pearce et al., 1999; Pearce et al., 2005a; Pearce et al., 2005b; Wray, 1999; North et al., 2005; Ratcliffe et al., 2004; Ratcliffe et al., 2006a; Ratcliffe et al., 2006b), and therefore there are few published accounts of broader stratigraphic studies that span numerous lithostratigraphic formations or groups (Ratcliffe et al., 2008).

DATA SET AND METHODOLOGY

Whole-rock geochemical data were acquired from the Upper Mannville Formation, the Basal Colorado Sandstone, and the Joli
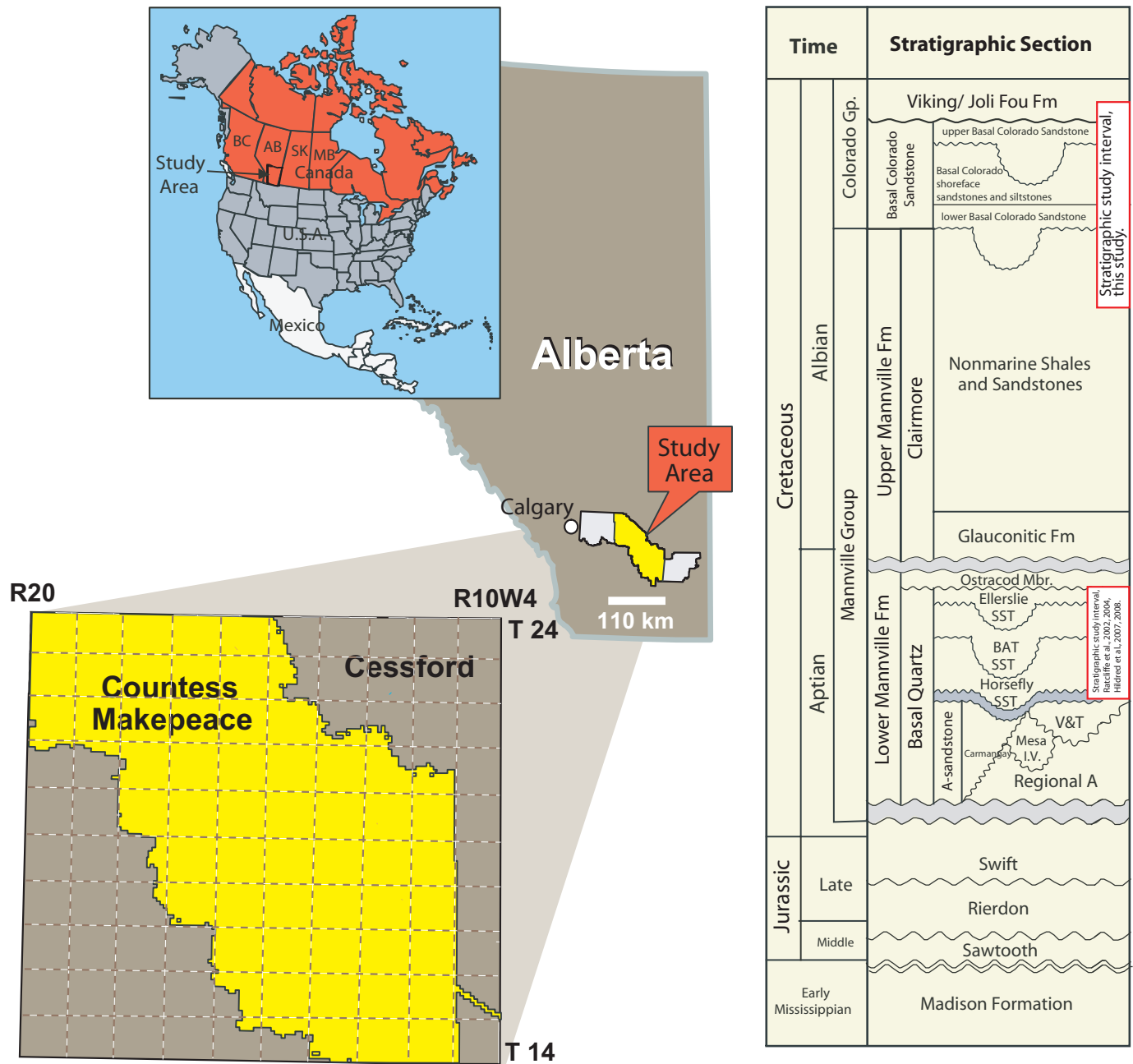
F̲ɪɢ. 1.—Location and stratigraphic position of study intervals, after Walker (2002) and Zaitlin et al. (2002).

Fou Formation (Fig. 2). A total of 122 core samples from five wells (Table 1) were analyzed using ICP-OES (inductively coupled plasma–optical emission spectroscopy) and ICP-MS (inductively coupled plasma–mass spectroscopy) analysis following alkali fusion preparation techniques as detailed in Jarvis and Jarvis (1995). These same preparation protocols and analytical methodologies were applied to the data acquired by Ratcliffe et al. (2004) and Hildred et al. (2007) from the Lower Mannville Formation. The samples were all analyzed on the same ICP-OES and ICP-MS instruments at Greenwich University (U.K.), and the data were drift corrected by the same individuals. Therefore, the whole-rock geochemical data from the Lower Mannville Formation presented by Ratcliffe et al. (2004) and Hildred et al. (2007) can be

directly compared to that acquired for this paper. Wells selected for analysis in this study are located between townships 14 and 24, and between ranges 10W4 and 20W4, from within Cessford and Countess–Makepeace pools (Fig. 1).

Geochemical Characterization

In any siliciclastic sequence, the primary differences in whole-rock geochemistry occur between lithologies (Ratcliffe et al., 2008). Sandstones, with their quartz-rich nature, have markedly different whole-rock geochemistry than clay-mineral-bearing mudrocks. Therefore, in order to recognize geochemical changes through time, within and between different lithostratigraphic
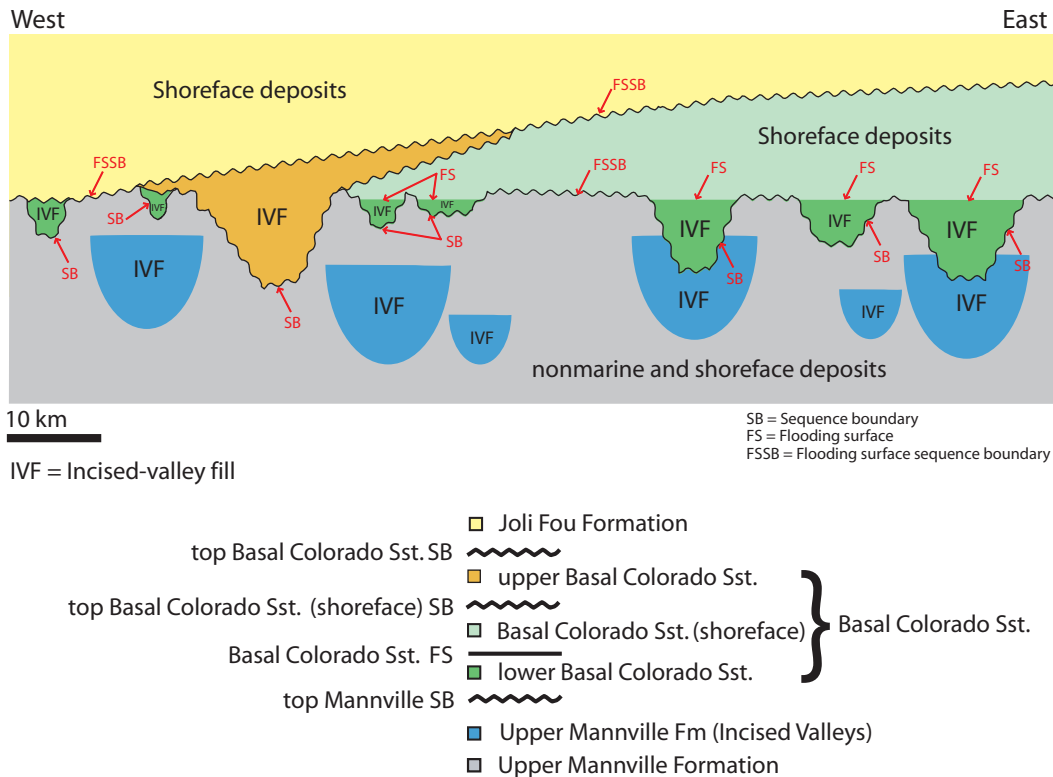
FIG. 2.—Schematic E-W cross section across Countess–Makepeace pool constructed to visually demonstrate the sequence stratigraphic architecture of the Upper Mannville Formation, the Basal Colorado Sandstone (informal unit), and the Joli Fou Formation, modified from Walker (2002). No vertical scale is implied on this cartoon; furthermore, this figure is to be viewed as a generalized E–W transect through the study area with no specific location.

TABLE 1.—Summary of study materials.

Well Code	Total silty mudstone samples	Stratigraphic assignment based on sedimentology	Number of samples assigned to each stratigraphic unit	Total sandstone samples	Stratigraphic assignment based on sedimentology	Number of samples assigned to each stratigraphic unit
7-26	8	Joli Fou Fm.	4	10	Joli Fou Fm.	3
		upper Basal Colorado Sst.	4		upper Basal Colorado Sst.	7
11-28	11	Joli Fou Fm	7	24	Basal Colorado Sst.	14
		Basal Colorado Sst.	4		U. Mannville Fm.	10
11-11	16	Joli Fou Fm.	3	5	U. Mannville Fm.	5
		Basal Colorado Sst.	7			
		U. Mannville Fm.	6			
2-08	13	Joli Fou Fm.	4	13	lower Basal Colorado Sst.	8
		Basal Colorado Sst.	5			
		lower Basal Colorado Sst.	1		U. Mannville Fm.	5
		U. Mannville Fm.	4			
3-14	5	Basal Colorado Sst.	5	17	Basal Colorado Sst.	2
					lower Basal Colorado Sst.	10
					U. Mannville Fm.	5

formations, mudstone and sandstone lithologies need to be considered separately. However, it is important to integrate interpretations from both lithologies to provide a holistic understanding of the chemostratigraphy.

Chemostratigraphic Characterization of Lithostratigraphic Units

Major changes in whole-rock geochemistry occur between each of the main lithostratigraphic units, the Lower Mannville Formation, the Upper Mannville Formation, and the Basal Colorado Sandstone (Figs. 3, 4). Although relatively few samples from the Joli Fou Formation have been analyzed (Figure 3), the mudstones of this formation are also geochemically distinct from older mudstones (Fig. 3C). Therefore, each of the lithostratigraphic units corresponds to a chemostratigraphic unit, which is here termed a chemostratigraphic package (CP) such that CP1 = Lower Mannville Formation, CP2 = Upper Mannville Formation, CP3 = Basal Colorado Sandstone, and CP4 = Joli Fou Formation (Figs. 3, 4). The chemical changes that enable characterization of CP1–CP4 can be considered as first-order variations. Furthermore, as demonstrated below, incised-valley-fill sandstones in CP1 and CP3 that have previously been demonstrated to be of different ages (Walker, 2002; Zaitlin et al., 2002), can be geochemically differentiated from one another and form second-order chemostratigraphic units in the study interval. These second-order chemostratigraphic units are here termed geochemical units (GU).
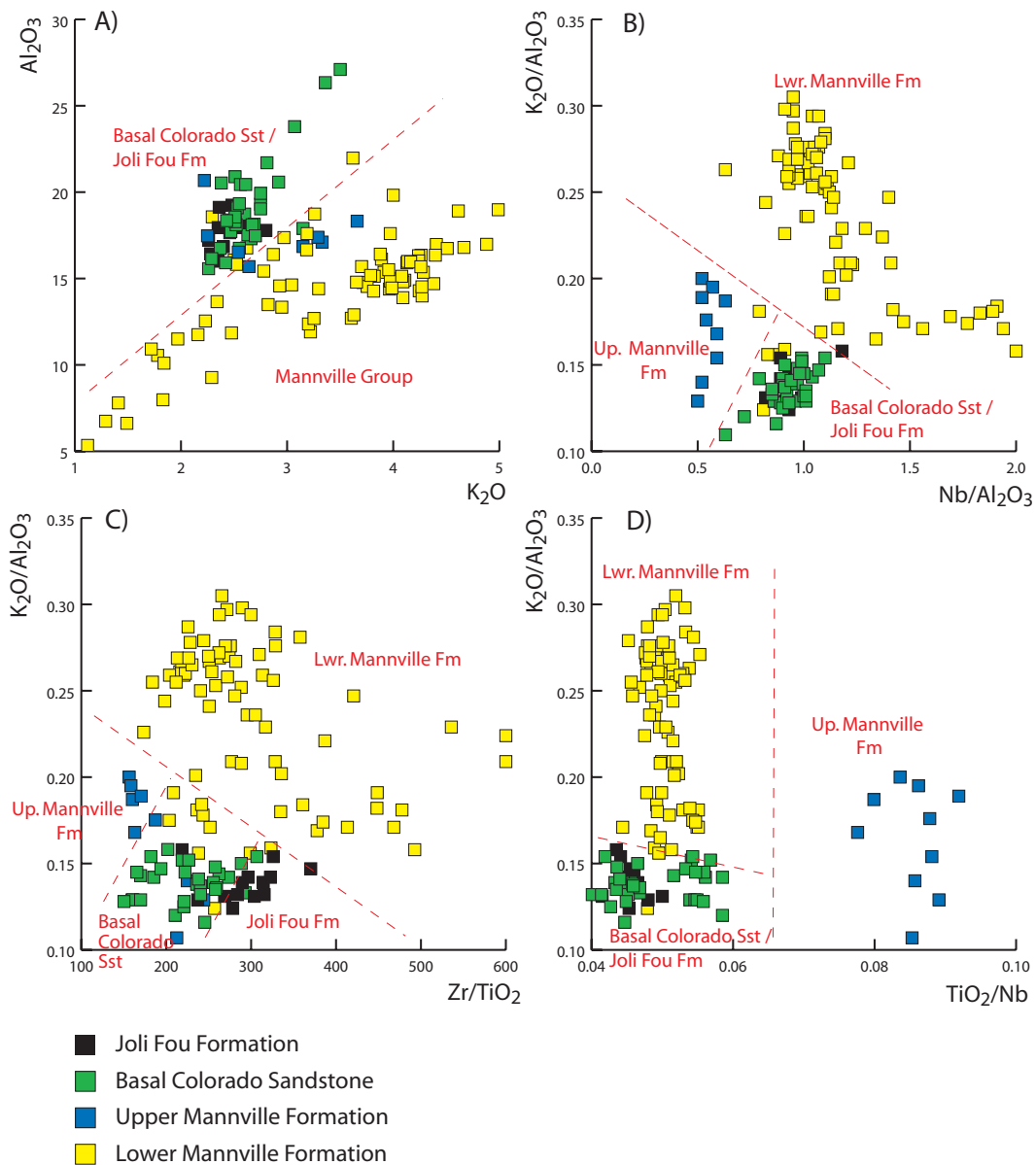

FIG. 3.—Binary diagrams constructed to demonstrate the whole-rock geochemical characterization of silty mudstones from the Lower Mannville Formation, the Upper Mannville Formation, the Basal Colorado Sandstone, and the Joli Fou Formation. All units are wt %.
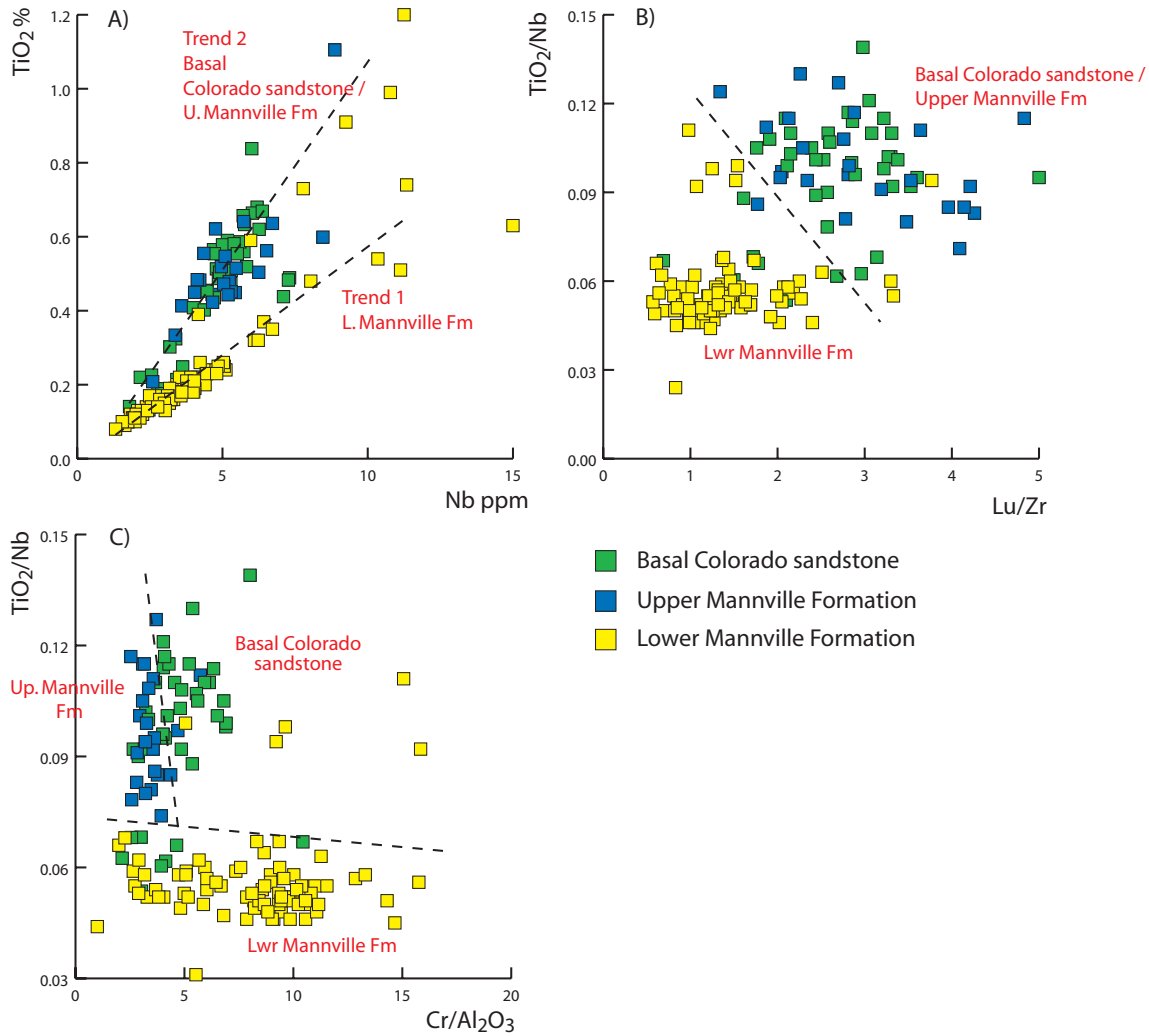
Fig. 4.—Binary diagrams constructed to demonstrate the whole-rock geochemical characterization of sandstones from the Lower Mannville Formation, the Upper Mannville Formation, and the Basal Colorado sandstone.

Mudstones.—

The Mannville Group mudstones have generally higher values of K_2O/Al_2O_3 ratio than those of the Basal Colorado Sandstone and the Joli Fou Formation (Fig. 3A). The mudstones of the Lower Mannville Formation are differentiated from those of the Upper Mannville Formation by their high Nb/Al_2O_3 values (Fig. 3B), high Zr/TiO_2 values (Fig. 3C), and low TiO_2/Nb values (Fig. 3D). The mudstones of the Basal Colorado Sandstone and the Joli Fou Formation are geochemically somewhat similar, with differentiation being achieved only by the marginally higher values of Zr/TiO_2 in the Joli Fou Formation (Fig. 3C). The similarity of the Joli Fou mudstones to mudstones from the underlying Basal Colorado Sandstones in terms of whole-rock geochemistry may reflect the fact that the lower parts of the Joli Fou Formation are reworked from the underlying sediments.

Sandstones.—

The Lower Mannville Formation sandstones have lower $TiO_2/$ Nb and Lu/Zr values than those of both the Upper Mannville

Formation and the Basal Colorado Sandstone (Fig. 4A, B). Figures 4A and 4B demonstrate that the most significant change in whole-rock geochemistry of the sandstones in the entire study sequence occurs between the Lower Mannville Formation and the Upper Mannville Formation, clearly providing a means to differentiate IVF sediments of the Lower Mannville Formation from the younger IVF rocks of the Upper Mannville Formations and Basal Colorado Sandstone. The change between the sandstones of the Upper Mannville Formation and the Basal Colorado Sandstone is more subtle and is described below.

*Upper Mannville Formation
and Basal Colorado Sandstone.—*

As demonstrated in Figure 4C, Upper Mannville Formation sandstones are differentiated from those of the Basal Colorado Sandstone by their relatively low Cr/Al_2O_3 values. However, the geochemical differentiation between these two formations is relatively subtle, with some degree of overlap in the TiO_2/Nb vs. Cr/Al_2O_3 binary plot and no clear separation between the samples. A more clearly defined geochemical break is seen on TiO_2 vs. Nb
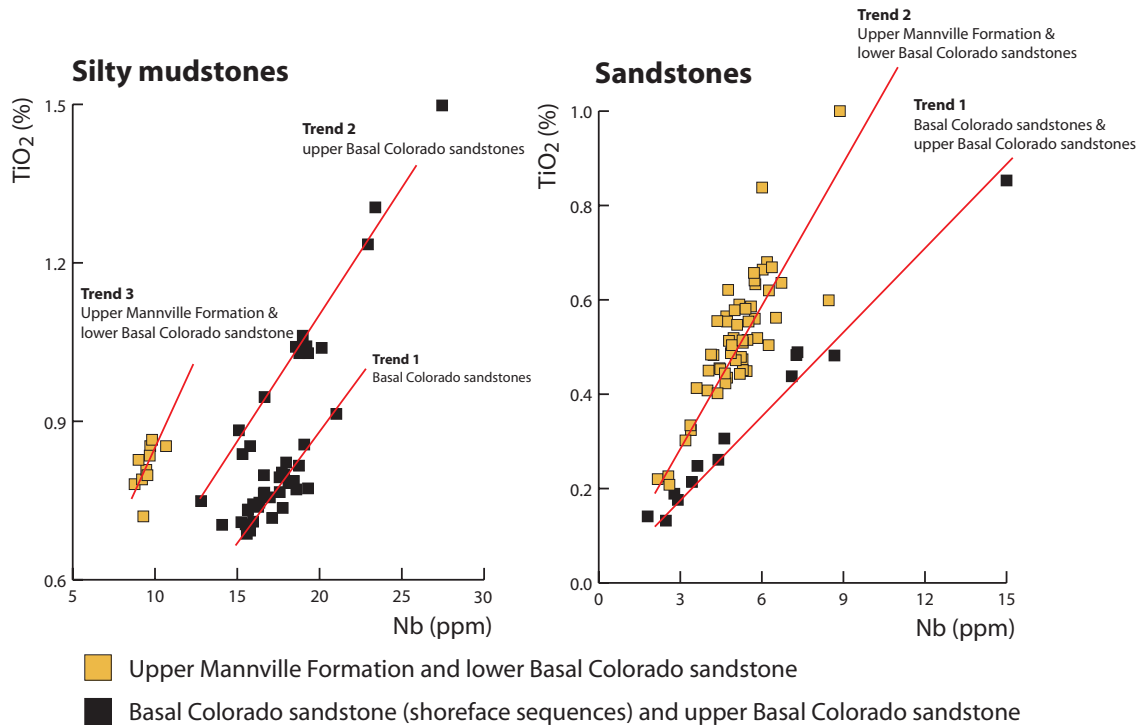
FIG. 5.—Binary diagrams constructed to demonstrate the whole-rock geochemical changes that took place in both silty mudstones and sandstones following deposition of the lower Basal Colorado sandstones.

binary diagrams (Fig. 5) due to the relatively high Nb values of both the sandstones and the mudstones of the Basal Colorado shoreface sandstones and the upper Basal Colorado sandstones compared to the equivalent lithologies of the Upper Mannville Formation and the lower Basal Colorado sandstone. Therefore, the change in geochemistry that results in the clear separation in Figure 5 occurs after deposition of the incised-valley-fill sediments of the lower Basal Colorado sandstone but before the onset of shoreface deposition that produced the Basal Colorado sandstone interval, and it affects both the sandstones and the mudstones.

Chemostratigraphic Characterization of Incised-Valley Sandstones from the Upper Mannville Formation and Basal Colorado Formation

Superimposed on the broad interformational changes in whole-rock geochemistry (described above) are a series of changes in other elemental ratios that allow high-resolution chemostratigraphic characterization of geochemical units within the Mannville Group and Basal Colorado Sandstone. Within each chemostratigraphic package, each geochemical unit is equivalent to an incised-valley-fill sequence of a different age. Similarly, the chemostratigraphic units of Ratcliffe et al. (2004) and Hildred et al. (2008), which equate to the Horsefly, the BAT, and the Ellerslie (Zaitlin et al., 2002), are second-order geochemical units in the Lower Mannville Formation (CP1). As displayed in Figure 2, there is a high potential for the juxtaposition of incised-valley-fill sandstones of markedly different ages to occur in the Upper Mannville Formation and the Basal Colorado Sandstone. The ability to clearly differentiate the valley-fill sandstones of each age using well-bore samples is important when constructing a sequence stratigraphic framework, since

the base of an IV is likely to be a sequence boundary, and being able to determine the relative ages of IVF sediments on either side of a sequence boundary is of paramount importance when constructing correlation frameworks.

The variations between the IVF sediments can be displayed by construction of "synthetic chemical logs" (*sensu* Ratcliffe et al., 2004) (Fig. 6) and by using binary and ternary graphical plots (Fig. 7).

Channel-fill sandstones of the Upper Mannville Formation are differentiated from those of the lower Basal Colorado sandstones by their relatively low TiO_2/Nb, Cr/Al_2O_3, and Cr/Nb values (Figs. 6, 7). They are readily differentiated from those of the upper Basal Colorado sandstones by their low K_2O/Al_2O_3 values. Sandstones of the lower Basal Colorado sandstones are differentiated from those of both the Upper Mannville Formation and the upper Basal Colorado Sandstone by high TiO_2/Nb, Cr/Al_2O_3, Cr/Nb, and P_2O_5/Al_2O_3 ratios (Figs. 6, 7). The sandstones of the upper Basal Colorado Sandstone are differentiated from those of the other two units by their high K_2O/Al_2O_3 values (Figs. 6, 7).

As demonstrated below, the controls on variation in the geochemistry that enable definition of both chemostratigraphic packages and geochemical units are related to changes in sediment provenance through time. In order to demonstrate this relationship between chemostratigraphic characterization and provenance, the likely controls on key elements in the sediments need to be understood.

MINERALOGY OF HEAVY MINERALS

Analyses were carried out to identify variations in heavy-mineral suites related to sediment provenance. Furthermore, since many heavy minerals have distinctive concentrations of
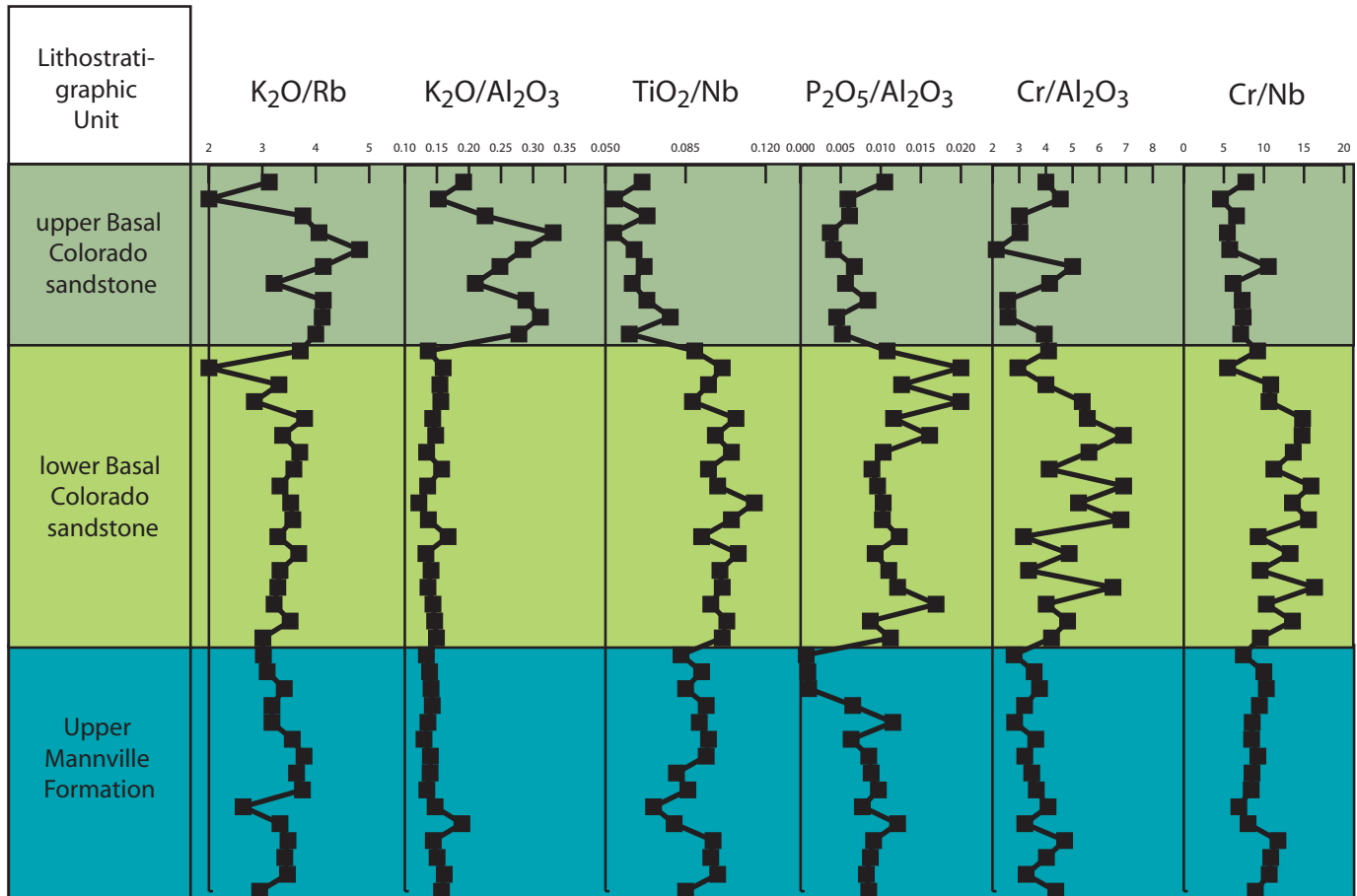
Fig. 6.—Synthetic chemical logs (after Ratcliffe et al., 2004) comprising core samples of sandstone lithologies from Upper Mannville Formation and the Basal Colorado Sandstone sections.

certain major and trace elements, the data obtained are ideally suited to better understand the factors controlling geochemical variations used for chemostratigraphic characterization (Fig. 8).

Although variations in the abundance of heavy minerals suggest changes in sediment provenance, heavy-mineral suites are not entirely controlled by source-rock mineralogy. Other processes, principally weathering, hydrodynamics, and diagenesis, may overprint the original provenance signal (Morton and Hallsworth, 1999). Such effects can be counteracted by examining ratios or indices of stable minerals with similar densities, because these indices are not affected by changes in hydraulic conditions during sedimentation or by diagenesis (Morton and Hallsworth, 1994). Table 2 displays the percentage of heavy-mineral species in each sample, and Table 3 displays the calculated indices for provenance-sensitive heavy minerals. The index ATi is defined as % apatite in total apatite plus tourmaline, GZi as % garnet in total garnet plus zircon, RZi as % Ti-oxide minerals in total Ti-oxide minerals plus zircon, RuZi as % rutile in total rutile plus zircon

MZi % monazite in total monazite plus zircon, and CZi as % chrome spinel in total chrome spinel plus zircon (after Morton and Hallsworth, 1994).

There is a marked change in the heavy-mineral suites between the Lower Mannville Formation and the Upper Mannville Formation, together with more subtle changes between the latter formation and the overlying Basal Colorado Sandstone (Fig. 8). The ATi, GZi, and CZi indices are all low in the Lower Mannville Formation, but higher in the units above. These changes in the heavy-mineral indices suggest a change from a predominantly metasedimentary provenance with some acid igneous influence during deposition of the Lower Mannville Formation to a provenance with a greater basic igneous influence in the Upper Mannville Formation and the Basal Colorado Sandstone. In terms of the geochemical dataset this change in provenance is reflected by an increase in Na_2O/K_2O values, which implies a relative increase in plagioclase compared to K-feldspar. A similar relationship between sediment provenance, feldspar types, and $Na_2O/$
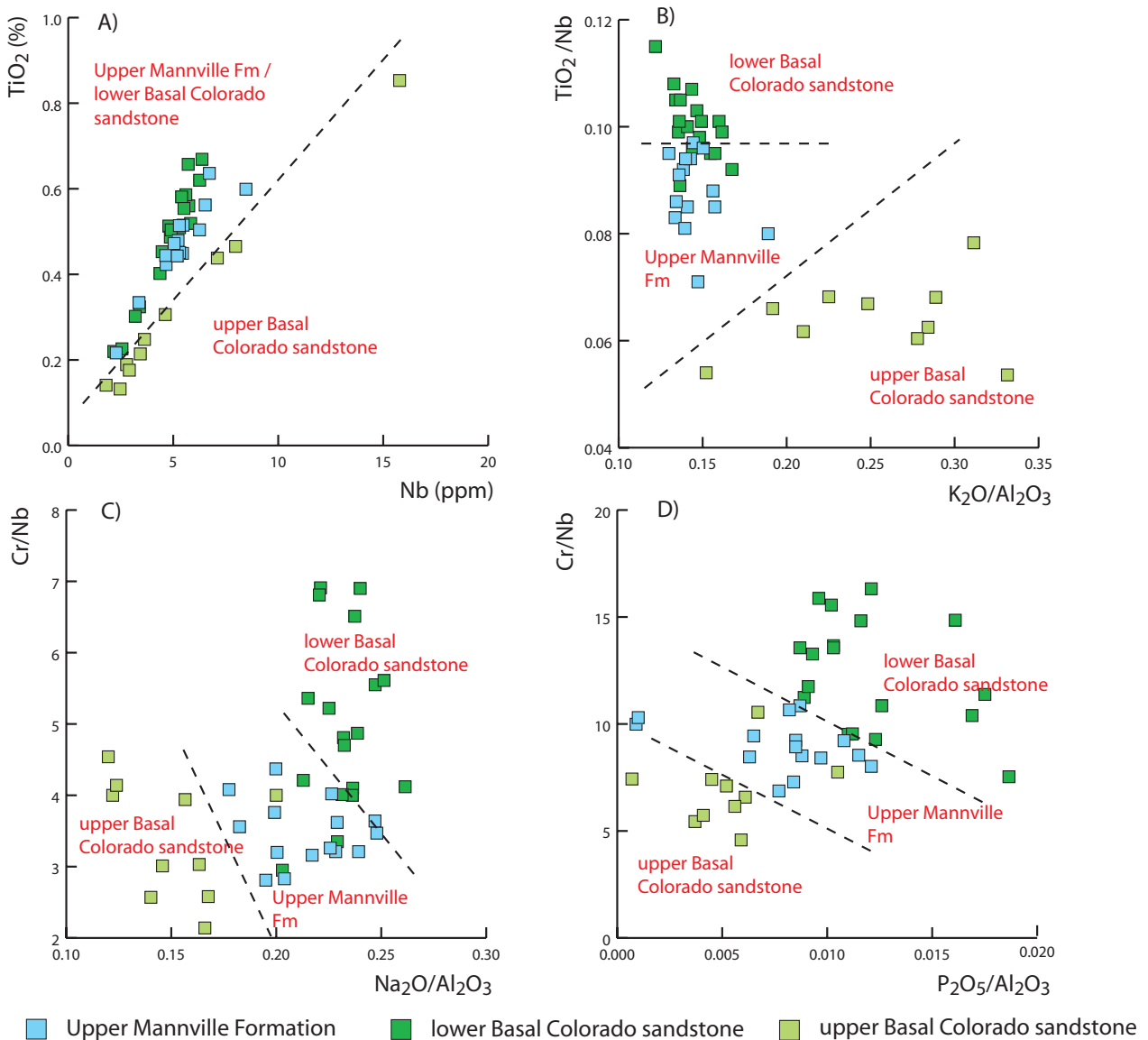
FIG. 7.—Binary diagrams constructed to demonstrate the whole-rock chemical characterization of Upper Mannville Formation and Basal Colorado sandstones (lower Basal Colorado sandstones and upper Basal Colorado sandstones).

K_2O values is reported from Miocene sandstones of the Kudankulam Formation in southern India (Armstrong et al., 2004).

Regional paleoflow during deposition of the Mannville Group was from south to north (Patchett et al., 2003); the change in sediment provenance at the Lower Mannville Formation–Upper Mannville Formation boundary is not directly related to a change in paleoflow direction. Therefore, the change must be related to a change in the sediment supply from the same hinterland (i.e., a change in the material being eroded within the catchment area, which is generally assumed to be the Rockies; Ross et al., 2005)

The Basal Colorado sandstones contain staurolite, a mineral not present in the Mannville Group. Due to its chemistry (Fe, Mg, Al silicate) and its relatively low abundance, it is a difficult mineral to model geochemically. However, it is indicative of a medium-grade regionally metamorphosed provenance, likely to

originally have been an argillaceous sediment prior to metamorphism (Deer et al., 1966). Paleoflow for the Basal Colorado Sandstone was from east to west (Potocki and Hutcheon, 1992), suggesting that the Canadian Shield was supplying the staurolite component of the heavy-mineral suite.

MINERALOGICAL SIGNIFICANCE OF SELECTED GEOCHEMICAL VARIATIONS

While chemostratigraphy *sensu stricto* is the characterization of sedimentary rocks in terms of changing geochemistry at a single location, it is of paramount importance to understand the controls on the whole-rock inorganic geochemistry before attempting to extend this zonation to create a chemostratigraphic correlation. This is important since it is evident that a correlation based upon, for example, variations in CaO values, which reflect
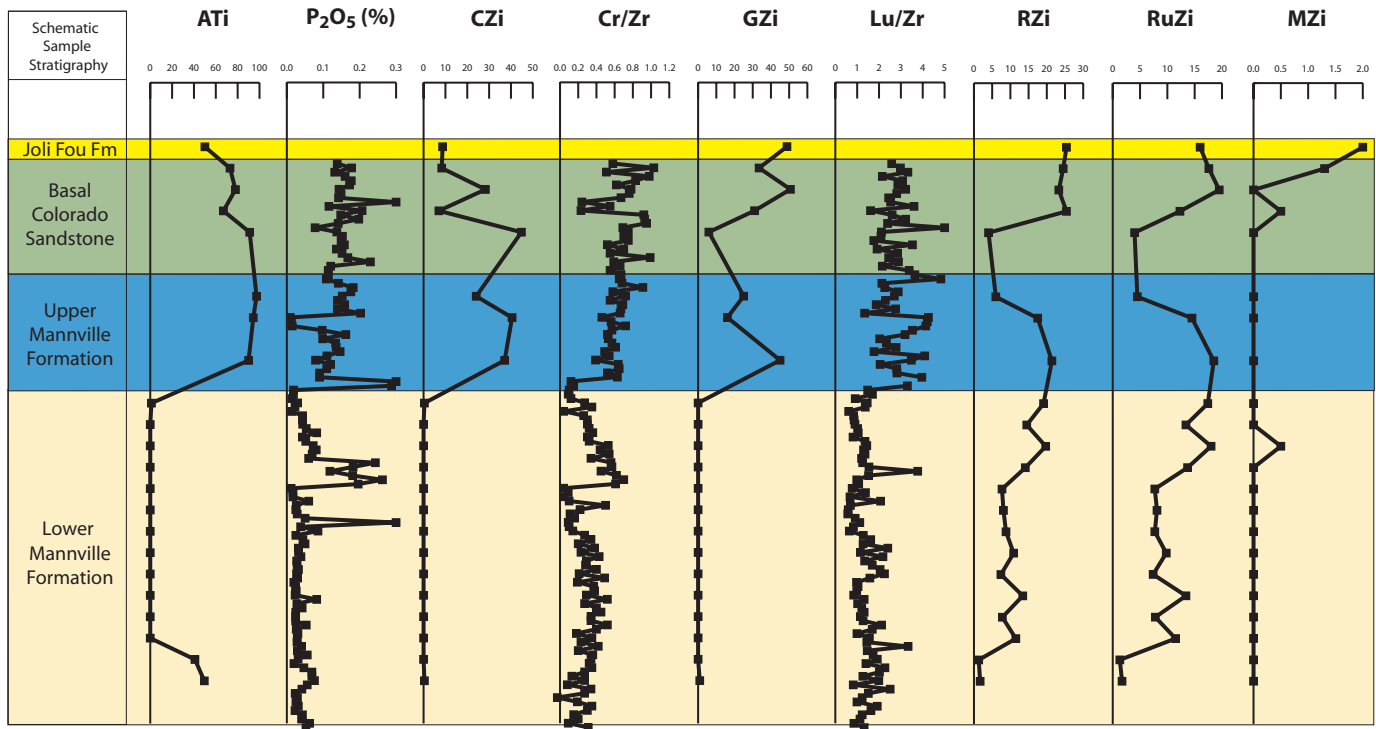
FIG. 8.—Heavy-mineral and whole-rock geochemical variations in the Lower Mannville Formation, the Upper Mannville Formation, and the Basal Colorado Sandstone. ATi, apatite:tourmaline index; GZi, garnet:zircon index; RZi, TiO_2 minerals:zircon index; RuZi, rutile:zircon index; MZi, monazite:zircon index; CZi, chrome spinel:zircon index (see Morton and Hallsworth, 1994, 1999, for definition of indices).

changes in calcite content of sediments, have significance to a correlation which is radically different from changes in Zr concentrations, which represent a change in the amount of zircon in the sample. To aid with this type of understanding, heavy-mineral analyses have been acquired from the Upper Mannville Formation and the Basal Colorado Sandstone. By comparing the distribution of these minerals with key elements and element ratios for sandstone lithologies it is possible to determine which elements reflect changes in sediment provenance, as opposed to diagenesis effects or simple lithology changes.

A relatively small subset of elements from the entire dataset acquired have been used for chemostratigraphic characterization, a common feature of chemostratigraphic studies (Pearce et al., 1999; Wray, 1999; Pearce et al., 2005a; Pearce et al., 2005b; Ratcliffe et al., 2004). The relationship of these elements and element ratios to mineralogy is considered below. In its strictest sense, chemostratigraphic correlation does not necessitate understanding the mineralogical controls on elements and element ratios, since the stratigraphic correlations produced are based on changes in whole-rock geochemistry. However, by trying to understand the controls on the key elements and element ratios, it is possible to extract additional geological information from chemostratigraphic correlations.

Mudstones

The elements and element ratios used to differentiate the mudstones in the study intervals here are Al_2O_3, K_2O, K_2O/Al_2O_3, Nb/Al_2O_3, TiO_2/Nb, and Zr/TiO_2 (Fig. 3). All of these elements and element ratios have been used to characterize the

mudstones of the Lower Mannville Formation by Ratcliffe et al. (2004) and Hildred et al. (2007). Those authors provide a detailed analysis of mineral-to-element relationships and have compared whole-rock geochemistry to XRD data and petrographic data. By extending the conclusions presented by Ratcliffe et al. (2004) into this study, the following controls on the key element and element ratios can be suggested.

Al_2O_3 and K_2O values are largely controlled by the abundance of clay minerals, and the K_2O/Al_2O_3 ratio is largely influenced by the illite / kaolinite ratio of the mudstones. Therefore, Figure 3A suggests that the Lower Mannville Formation has a higher illite/kaolinite ratio than the Upper Mannville Formation, Basal Colorado Sandstone, and Joli Fou Formation, i.e., higher K_2O/Al_2O_3 values (Fig. 3B).

Zr and TiO_2 are both related principally to silt-grade heavy-mineral grains, zircon being associated with zircons and TiO_2 with Ti-oxides such as rutile and anatase. Therefore, Zr/TiO_2 (Fig. 3C) reflects the zircon/(rutile + anatase) ratio and an overall increase in the ratio from the Lower Mannville Formation, through the Basal Colorado Sandstone into the Joli Fou Formation.

The exact control on Nb concentrations remains somewhat enigmatic. The linear relationship between the element and TiO_2 in Figure 4A implies that it is related to Ti-bearing minerals in the sandstones. However, mudstones from the Upper Mannville Formation are clearly relatively enriched in a Ti-bearing mineral that does not have the same proportion of Nb as the Ti-bearing minerals of other units (Fig. 3D). The exact control on the TiO_2/Nb ratio cannot therefore be deduced, but it acts as a very clear defining ratio for the Upper Mannville Formation mudstones.

TABLE 2.—Summary of heavy-mineral results. All minerals are reported as a percentage. St = Anatase, Ap = Apatite, Ct = chloritoid, Cr = chrome spinel, Gt = garnet, Mo = Monazite, Ru = rutile, St = staurolite, To = tourmaline, Zr = zircon.

Data Origin	Well Code	Depth (m)	Formation	At	Ap	Ct	Cr	Gt	Mo	Ru	St	To	Zr
Samples analyzed as part of this study	7/26	851.92	Joli Fou Formation	4.0	22.5	1.0	1.0	17.5	1.0	4.5	5.0	22.0	21.5
	7/26	854.35	upper Basal Colorado Sst.	3.0	48.0	1.5	1.0	8.0	0.5	3.5	1.0	15.5	18.0
	7/26	857.40	upper Basal Colorado Sst.	R	56.0	1.0	5.0	9.5	0.0	2.0	1.0	16.5	9.0
	3/14	930.20	lower Basal Colorado Sst.	3.5	32.5	R	2.0	12.5	R	3.5	5.0	19.5	21.5
	11/28	910.90	lower Basal Colorado Sst.	1.0	56.0	0.0	14.0	1.5	0.0	1.0	0.0	5.5	21.0
	3/14	935.70	U. Mannville Fm	0.6	61.9	0.0	6.7	6.7	0.0	1.1	0.0	1.7	21.3
	11/28	920.65	U. Mannville Fm	1.0	48.5	0.0	16.0	4.5	0.0	4.0	0.0	3.0	23.0
	11/28	923.20	U. Mannville Fm	0.7	54.3	0.0	8.7	12.1	0.0	3.4	0.0	6.0	14.8
Data originally analyzed and published in Ratcliffe et al. (2004)	10-29-36-27-W4	1889.15	L. Mannville Fm	1.0	1.0	0.0	R	0.0	0.0	5.5	0.0	67.0	25.5
	10-29-36-27-W4	1891.28	L. Mannville Fm	1.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	63.0	33.5
	10-29-36-27-W4	1894.33	L. Mannville Fm	1.0	0.0	0.0	0.0	0.0	0.5	8.5	0.0	53.5	36.5
	10-29-36-27-W4	1895.86	L. Mannville Fm	R	0.0	0.0	0.0	0.0	0.0	8.0	0.0	42.0	50.0
	10-29-36-27-W4	1901.34	L. Mannville Fm	0.0	0.0	0.0	0.0	0.0	0.0	5.0	0.0	37.0	58.0
	10-29-36-27-W4	1903.48	L. Mannville Fm	0.0	0.0	0.0	0.0	0.0	0.5	5.0	0.0	36.5	58.0
	6-11-26-28-W4	2131.0	L. Mannville Fm	1.0	0.0	0.0	0.0	0.0	0.0	6.5	0.0	16.0	76.5
	6-11-26-28-W4	2135.0	L. Mannville Fm	1.0	0.0	0.0	0.0	0.0	0.0	8.0	0.0	16.5	74.5
	6-11-26-28-W4	2140.0	L. Mannville Fm	0.0	0.0	0.0	0.0	0.0	0.0	5.0	0.0	7.0	88.0
	6-11-26-28-W4	2148.0	L. Mannville Fm	0.5	0.0	0.0	0.0	0.0	0.0	10.5	0.0	16.5	72.5
	6-11-26-28-W4	2150.0	L. Mannville Fm	0.0	0.0	0.0	0.0	0.0	0.0	6.5	0.0	18.0	75.5
	6-11-26-28-W4	2152.0	L. Mannville Fm	0.5	0.0	0.0	R	0.0	0.0	7.0	0.0	36.5	56.0
	1-35-1-20-W4	1174.09	L. Mannville Fm	0.0	4.0	0.0	0.0	0.0	1.0	1.5	0.0	6.0	87.5
	1-35-1-20-W4	1178.97	L. Mannville Fm	0.0	5.5	0.0	R	1.0	0.0	1.5	0.0	9.0	83.0

TABLE 3.—Provenance-sensitive heavy-mineral indices (Morton and Hallsworth, 1994).

Data Origin	Well Code	Depth (m)	Formation	ATi	GZi	RZi	RuZi	MZi	CZi
Samples analyzed as part of this study	7/26	851.92	Joli Fou Formation	50.0	48.8	25.4	16.0	2.0	8.7
	7/26	854.35	upper Basal Colorado Sst.	73.0	33.5	24.5	17.6	1.3	8.3
	7/26	857.40	upper Basal Colorado Sst.	78.0	50.7	23.3	19.5	0.0	28.3
	3/14	930.20	lower Basal Colorado Sst.	67.0	31.0	25.4	12.3	0.5	7.0
	11/28	910.90	lower Basal Colorado Sst.	91.0	5.9	4.0	4.0	0.0	44.8
	3/14	935.70	U. Mannville Fm	97.3	25.0	6.0	4.5	0.0	24.1
	11/28	920.65	U. Mannville Fm	94.3	16.1	17.5	14.5	0.0	40.5
	11/28	923.20	U. Mannville Fm	90.0	45.0	21.4	18.5	0.0	37.1
Data originally analyszd and published in Ratcliffe et al. (2004)	10-29-36-27-W4	1889.15	L. Mannville Fm	1.1	0.0	19.1	17.4	0.0	0.4
	10-29-36-27-W4	1891.28	L. Mannville Fm	0.0	0.0	14.5	13.4	0.0	0.0
	10-29-36-27-W4	1894.33	L. Mannville Fm	0.0	0.0	19.7	18.0	0.5	0.0
	10-29-36-27-W4	1895.86	L. Mannville Fm	0.0	0.0	14.1	13.7	0.0	0.0
	10-29-36-27-W4	1901.34	L. Mannville Fm	0.0	0.0	7.7	7.7	0.0	0.0
	10-29-36-27-W4	1903.48	L. Mannville Fm	0.0	0.0	8.1	8.1	0.0	0.0
	6-11-26-28-W4	2131.0	L. Mannville Fm	0.0	0.0	8.8	7.7	0.0	0.0
	6-11-26-28-W4	2135.0	L. Mannville Fm	0.0	0.0	10.9	9.8	0.0	0.0
	6-11-26-28-W4	2140.0	L. Mannville Fm	0.0	0.0	7.4	7.4	0.0	0.0
	6-11-26-28-W4	2148.0	L. Mannville Fm	0.0	0.0	13.4	13.4	0.0	0.0
	6-11-26-28-W4	2150.0	L. Mannville Fm	0.0	0.0	7.8	7.8	0.0	0.0
	6-11-26-28-W4	2152.0	L. Mannville Fm	0.0	0.0	11.5	11.5	0.0	0.0
	1-35-1-20-W4	1174.09	L. Mannville Fm	40.9	0.0	1.3	1.3	0.0	0.0
	1-35-1-20-W4	1178.97	L. Mannville Fm	49.5	0.9	1.7	1.7	0.0	0.4

Sandstones

Ratcliffe et al. (2004) present heavy-mineral data from sandstones of the Lower Mannville Formation, but they do not present whole-rock geochemical data for the sandstones, making direct comparison of the heavy mineralogy and whole-rock geochemistry difficult. Here, the heavy-mineral data acquired by Ratcliffe et al. (2004) are combined with data acquired in this study. Furthermore, whole-rock inorganic geochemical data acquired by Hildred et al. (2007) are used to supplement the geochemical data presented here. By combining these various datasets, heavy-mineral compositions can be compared directly with whole-rock geochemical data for the Mannville Group and the Basal Colorado Sandstone (Fig. 8).

Figure 8 demonstrates that there is a close similarity between changes in the provenance-sensitive heavy-mineral indices and selected elements and element ratios that have been used to chemostratigraphically characterize the formations. Phosphorus concentrations chiefly reflect the higher apatite contents and therefore higher ATi values in the Upper Mannville Formation and the Basal Colorado Sandstone. The Cr/Zr ratio mimics the CZi heavy mineral due to the relationship between Cr concentrations and Cr-spinel and Zr concentrations and zircon. A similar relationship between Zr, Cr, zircon, and Cr-spinel in sandstones is reported by Singh and Rajamani (2001), Armstrong et al. (2004), and Ratcliffe et al. (2008). The Lu/Zr ratio displays a close relationship with the GZi index. Garnets are commonly relatively enriched in heavy rare earth elements such as Lu when compared to zircons (Henderson, 1984). Therefore the Lu/Zr ratio emphasizes heavy minerals, such as garnet, that have high concentrations of heavy rare earth element. A similar relationship between Lu/Zr and garnet distribution is reported by Ratcliffe et al. (2006b)

TiO_2 and Nb are two elements that commonly occur together in a range of minerals, such as Ti-oxide heavy minerals, clay minerals, and volcanogenic material (Deer et al., 1966). Commonly, they display a positive linear relationship in sediments, as demonstrated in Figure 5. When there is development of two distinctive linear trends between the two elements, as is the case in Figure 5, the implication is that there has been a change in the mineralogy.

DISCUSSION

Although chemostratigraphy is a relatively new stratigraphic methodology, there are an increasing number of publications dealing with the use of inorganic geochemical data for stratigraphic correlation (Pearce et al., 1999, Pearce et al., 2005a, Pearce et al., 2005b, Ratcliffe et al., 2006, Ratcliffe et al., 2008). However, its application has, to some extent, developed in an ad hoc manner. Here, a more structured approach is adopted: defining broad isochemical intervals, termed chemostratigraphic packages, that are in turn composed of finer-resolution isochemical intervals termed geochemical units. Such a hierarchical approach is desirable in any stratigraphic correlation and is an approach adopted for other, more established stratigraphic techniques, such as lithostratigraphy, sequence stratigraphy, and chronostratigraphy.

Ideally, when defining a chemostratigraphic characterization in a basin, chemostratigraphic packages should be features that can be recognized over relatively wide geographic areas, thereby providing the basis for a basin-wide stratigraphic correlation framework. Geochemical units can be more localized features, thereby providing a level of detail to the stratigraphic architecture of each chemostratigraphic package. In order to decide which isochemical intervals are potentially packages and which are more likely to be localized geochemical units, it is imperative to understand the mineralogical and therefore geological controls on the elements and element ratios used in a chemostratigraphic characterization.

As demonstrated herein, changes in whole-rock geochemistry that occur between the chemostratigraphic packages identified are to a large extent likely to be controlled by changes in sediment provenance, and can therefore be thought of as relatively laterally continuous chemical features. The change from south-derived sediments during deposition of the Mannville Group (CP1 and CP2) and a more eastern source of sediments during deposition of the Basal Colorado Sandstone (CP3) has been documented (Potocki and Hutcheon, 1992; Ross et al., 2005). However, the geochemical data and heavy-mineral analyses suggest that a marked change in provenance also took place between deposition of the Lower Mannville Formation (CP1) and the Upper Mannville Formation (CP2), despite the entire Mannville Group being sourced from the south. Therefore, this major change in provenance can be attributed only to a change in the material being sourced from the hinterland to the south. The Joli Fou Formation (CP4) represents the onset of a major transgression from the south, with sediment being derived largely from the west, resulting in the markedly different geochemistry of the Joli Fou Formation compared to the underlying units (Potocki and Hutcheon, 1992).

Changes in whole-rock geochemistry which allow the identification of geochemical units in this study are to a large extent likely to be controlled by more subtle changes in sediment provenance, changes in paleoclimate, and changes in facies (Ratcliffe et al., 2004; Hildred et al., 2008), all of which are potentially more localized features that may not be correlative over large distances.

Furthermore, by integrating the chemostratigraphic characterizations with other disciplines, additional information can be obtained from the whole-rock geochemical dataset. As discussed above, Ratcliffe et al. (2004) integrated their dataset on the Lower Mannville with heavy-mineral stratigraphy to better understand sedimentary provenance. While in Ellwood et al. (2008) whole-rock geochemical data were combined with magnetic-susceptibility stratigraphy in order to characterize the Cretaceous–Tertiary Global Boundary Stratotype Section and Point. Here, it has been demonstrated that in cored intervals where sandstone-on-sandstone erosional contacts occur, chemostratigraphy can be used to determine if that surface is a localized scour surface or is the base of a significant incised-valley feature and therefore a sequence boundary (Fig. 9). Hence, the chemostratigraphic interpretations can be integrated into sequence stratigraphic models.

CONCLUSIONS

Chemostratigraphic techniques applied to the Mannville Group and the Basal Colorado Sandstone provide a means to characterize each major lithostratigraphic unit by use of changes in the whole-rock geochemistry of sandstones and mudstones. The changes in geochemistry that enable these chemostratigraphic packages to be characterized are a result of changes in heavy and detrital mineralogy of the sandstones and silty mudstones, which in turn reflect variation in sediment source through time.

The changes that enable definition of chemostratigraphic packages are considered first-order variations in whole-rock geochemistry. Superimposed on these first-order changes are a series of second-order variations in whole-rock geochemistry that enable characterization of geochemical units. The geochemi-
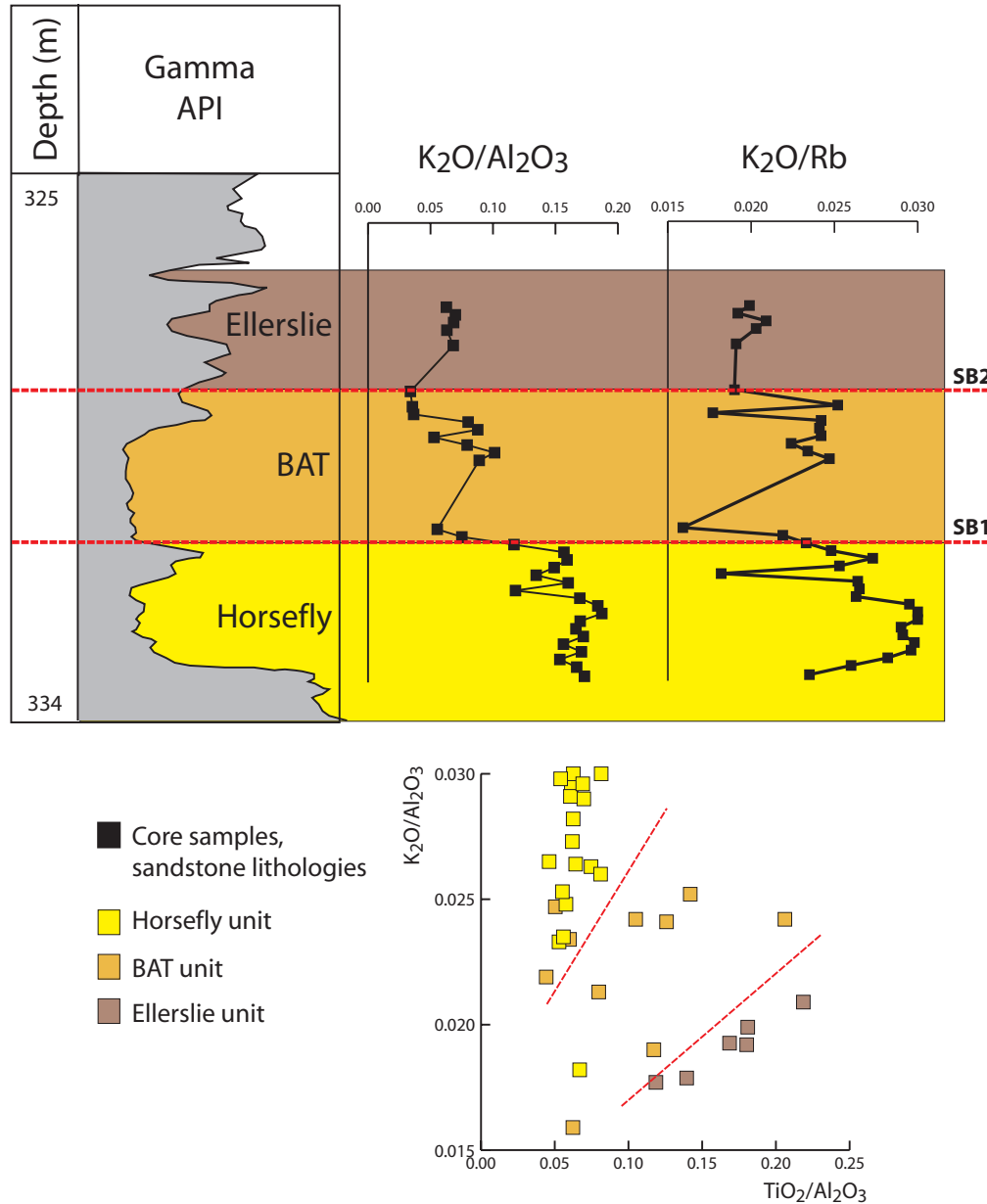
FIG. 9.—Whole-rock geochemical data used to differentiate incised-valley-fill sediments within a single well bore (15-32-10-18W4) comprising Horsefly, BAT, and Ellerslie units of the Basal Quartz (Hildred et al., 2008)

cal units represent incised-valley-fill sediments from Upper Mannville Formation channels, Lower Basal Colorado sandstones, and upper Basal Colorado sandstones. Similarly, each of the incised-valley successions geochemically characterized by Ratcliffe et al. (2004) and Hildred et al. (2008) in the Lower Mannville Formation, namely Horsefly, BAT, and Ellerslie units, are also geochemical units identified by second-order variations in geochemistry (Fig. 9).

By enabling incised-valley sediments of different ages to be recognized and differentiated, even where incised-valley-fill sandstones are juxtaposed in a well bore, the technique of chemostratigraphy provides a means to better identify and correlate sequence boundaries in low-accommodation fluvial environments. Furthermore, chemostratigraphy has been demon-

strated to be a hierarchical stratigraphic technique that has application in lithostratigraphic methodologies to independently characterize lithostratigraphic formations and units.

ACKNOWLEDGMENTS

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