Chemostratigraphy and depositional environment of an Ordovician sedimentary section across the Miramichi Group - Tetagouche Group contact, northeastern New Brunswick

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A thick section of Ordovician sedimentary rocks underlies and overlies felsic to mafic volcanic rocks of the Tetagouche Group, Bathurst Mining Camp. The dark grey quartzose slates and siltstones of the Patrick Brook Formation (Miramichi Group) occur below the volcanic rocks, whereas the dark grey to black slates and siltstones of the Boucher Brook Formation (Tetagouche Group) are intercalated with the volcanic rocks and overlie the sequence. The Miramichi-Tetagouche contact represents the interpreted Gander-Dunnage boundary in northeastern New Brunswick. Distinguishing between these two similar formations is important for stratigraphic and geotectonic interpretations of the Bathurst Mining Camp and for exploration in these sequences. The geochemical composition of a semi-conformable section of rocks from the Boucher Brook (Middle to Late? Ordovician) and Patrick Brook (Early to Middle Ordovician) formations was determined to identify geochemical chemostratigraphic discriminants, as well as to determine the depositional environment in which these were deposited.

The high Al_2O_3 and distinctly higher high-field-strength elements (LREE, Th, HREE, and Y) in the Patrick Brook rocks are characteristic of mature sedimentary rocks and indicate intense chemical weathering (tropical environment) in the source regions, which is consistent with their compositional similarity to Avalon-derived shales analogous to Gander Zone sedimentary rocks. The Boucher Brook slates and siltstones are immature sedimentary rocks based on the preservation of albite and the less coherent trace-element systematics to phyllosilicate indices (Al_2O_3 and K_2O). The Boucher Brook Formation is probably derived from the associated volcanic rocks.

The higher Mn and Fe and positive Ce/Ce* anomaly in some Boucher Brook Formation compared to the Patrick Brook rocks indicate that the Boucher Brook rocks in this section were deposited in a transitional anoxic/oxic environment. The Patrick Brook rocks that immediately precede felsic volcanism and formation of massive sulphide deposits are highly reduced based on C and S contents, which is consistent with the sulphur isotope data. Moderately heavy $\delta^{34}S$ values are indicative of SO_4^{2-} reduction to H_2S under anoxic conditions, which is significant in the formation and preservation of massive sulphides in the basal Tetagouche sequence.

Une section épaisse de roches sédimentaires de l'Ordovicien est sus-jacente et sous-jacente à des roches volcanomafiques à volcanofelsiques du groupe de Tetagouche, dans le Camp minier de Bathurst. Des siltstones et des schistes quartzeux gris foncé de la Formation de Patrick Brook (groupe de Miramichi) sont présents au-dessous des roches volcaniques, tandis que des schistes et des siltstones gris foncé à noirs de la formation de Boucher Brook (groupe de Tetagouche) sont intercalés dans les roches volcaniques et recouvrent la séquence. La surface de contact de Miramichi-Tetagouche représente ce qu'on interprète comme la limite de Gander-Dunnage dans le nord-est du Nouveau-Brunswick. Il est important d'établir une distinction entre ces deux formations semblables pour les interprétations stratigraphiques du Camp minier de Bathurst et pour l'exploration dans ces séquences. On a déterminé la composition géochimique d'une section semi-concordante de roches de Boucher Brook (Ordovicien moyen à tardif?) et de Patrick Brook (Ordovicien inférieur à moyen) afin de repérer les discriminants chimiostratigraphiques géochimiques ainsi que pour définir le milieu sédimentaire dans lequel ceux-ci ont été déposés.

La quantité prononcée d'Al_2O_3 et la présence distinctement supérieure d'éléments d'intensité de champ élevée (éléments de terres rares légers, Th, éléments de terres rares lourds et Y) dans les roches de Patrick Brook constituent des traits caractéristiques de roches sédimentaires matures; elles témoignent d'une altération climatique chimique intense (milieu tropical) dans les régions d'origine, ce qui est compatible avec la similarité de leur composition avec les schistes en provenance d'Avalon analogues aux roches sédimentaires de la zone de Gander. Les schistes et les siltstones de Boucher Brook sont des roches sédimentaires immatures basées sur la conservation d'albite et la corrélation d'éléments traces moins cohérents avec les indices de phyllosilicates (Al_2O_3). La Formation de Boucher Brook provient probablement de roches volcaniques connexes.

La proportion supérieure de Mn et de Fe et l'anomalie positive de Ce/Ce* dans certaines parties de la Formation de Boucher Brook révèlent que les roches de Boucher Brook de cette section ont été déposées dans un milieu anoxique / oxique de transition. Les roches de Patrick Brook qui ont immédiatement précédé le volcanisme felsique

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et la formation de gîtes de sulfures massifs ont, à en juger par leur teneur en C et en S, subi une réduction importante, ce qui correspond aux données isotopiques relatives au soufre. Les valeurs moyennement prononcées de $\delta^{34}S$ témoignent d'une réduction du SO_4^{2-} en H_2S dans des conditions anoxiques, un phénomène déterminant dans la formation et la conservation des sulfures massifs dans la séquence basale de Tetagouche.

[Traduit par la rédaction]

INTRODUCTION

Within the Bathurst Mining Camp, the Patrick Brook and Boucher Brook formations contain slate and siltstone with lesser amounts of sandstone. The Patrick Brook Formation represents the top of the Lower to Middle Ordovician Miramichi Group and the Boucher Brook Formation forms the top of the Middle to Upper Ordovician Tetagouche Group that hosts one of the most productive base-metal mining camps in the world (McCutcheon, 1992; van Staal *et al.*, 1992). The mature quartzitic wackes, siltstones and sandstones of the Miramichi Group have been interpreted as equivalent to the sedimentary rocks of the Gander Zone, whereas the Tetagouche Group, including the Boucher Brook sedimentary rocks, are correlated with the Dunnage Zone in Newfoundland (van Staal and Fyffe, 1991). The Llandeilian-Caradocian black shales (paleontological graptolite control) and cherts of the Boucher Brook Formation resemble the black shales and cherts that blanket the Exploits subzone (Dunnage Zone) in Newfoundland (see references in van Staal and Fyffe, 1991; Currie, 1995). The Patrick Brook and Boucher Brook formations are texturally similar making them difficult to distinguish in structurally complex areas where characteristic lithotypes are absent and/or outcrop is sparse. This is further complicated by the heterogeneous strain (low to high) observed in these rocks, particularly in the shale horizons, local evidence of tectonic mélange, and the lower to middle greenschist metamorphic grade (fine grained, muscovite-chlorite-quartz assemblage) in the area. The difficulty in distinguishing Patrick Brook from Boucher Brook rocks has impeded stratigraphic and structural interpretations in many parts of the Bathurst Camp, but initial work by Fyffe (1994) has suggested that there are some differences in their respective HFS- and hydrogeneous/hydrothermal-element contents.

Recently, an exploration drill hole (DDH BC94-2) intersected a semi-conformable section containing appreciable thicknesses of both the Boucher Brook and Patrick Brook formations. Drill core from this hole was systematically sampled in order to test Fyffe's (1994) preliminary findings vis-a-vis geochemical differences between these two formations. This paper describes the results of this geochemical study and identifies several geochemical discriminants that may help to distinguish between Boucher Brook and Patrick Brook slates and siltstones. Furthermore, the lithogeochemistry provides information about the local environment in which each was deposited. This study is the first phase of a larger project aimed at defining chemostratigraphic indices and palaeodepositional environments of these two formations and how they relate to the formation of massive sulphide deposits.

GEOLOGICAL CONSIDERATIONS

Introduction

The drill hole (BC94-2) section that was examined and sampled was collared in rocks of the Boucher Brook Formation and drilled east at 56° dip through what appears to be aphyric rhyolite of the Flat Landing Brook Formation into the Patrick Brook Formation (Figs. 1, 2, 3; Moore, 1993; Hoy, 1994). The angle of bedding to the core axis is approximately 45° near the collar and with the outcrop information indicates an average dip of 80°W for the stratigraphy. This stratigraphic section is unique for two reasons: first, the entire sequence appears conformable and second, there is only a thin rhyolite, which is discontinuous along strike, separating the Patrick Brook and Boucher Brook formations in this area. The volcanic part of the section section consists of a weakly sericitized aphyric rhyolite (<54 m thick) typical of the Flat Landing Brook Formation, i.e., the Nepisiguit Falls volcaniclastic rocks and Boucher Brook alkaline mafic volcanic rocks are absent. Therefore, there is lesser influence of local volcanism and hydrothermal alteration on the sediment geochemistry. To the south, the section is conformable based on the presence of synvolcanic dykes that cross-cut the sequence at the Brunswick No. 12 deposit (Lentz and van Staal, 1995). This is also confirmed by the few pebbles of aphyric rhyolite in the overlying Boucher Brook sequence evident in drill core, as well as large Patrick Brook siltstone clasts in the basal Nepisiguit Falls Formation to the north at Little Falls (cf. Fyffe, 1976; Rice and van Staal, 1992). The age relationships and constraints of the rock units compared to the standard stratigraphic column for the Bathurst Camp are shown on Figure 2 (van Staal and Fyffe, 1991; Fyffe, 1994) for comparison. Descriptions of the Patrick Brook and Boucher Brook formations follow; descriptions of the other rock units making up the Bathurst Camp can be found in van Staal and Fyffe (1991), van Staal *et al.* (1992), and McCutcheon *et al.* (1993).

Patrick Brook Formation (Miramichi Group)

The type locality is near the mouth of Patrick Brook on the Tetagouche River just north of the study area. It is characterized by epiclastic dark grey, thin- to thick-bedded sandstones, which are interlayered with grey slates, siltstones, and wackes (van Staal *et al.*, 1992). The sandstones typically contain black volcanic quartz phenoclasts greater than 5% of the mode (McCutcheon *et al.*, 1993). Rice and van Staal (1992) described volcanic quartz (>5%), local grading, and ripple cross-lamination in the Patrick Brook Formation, which were also locally present here. The age of

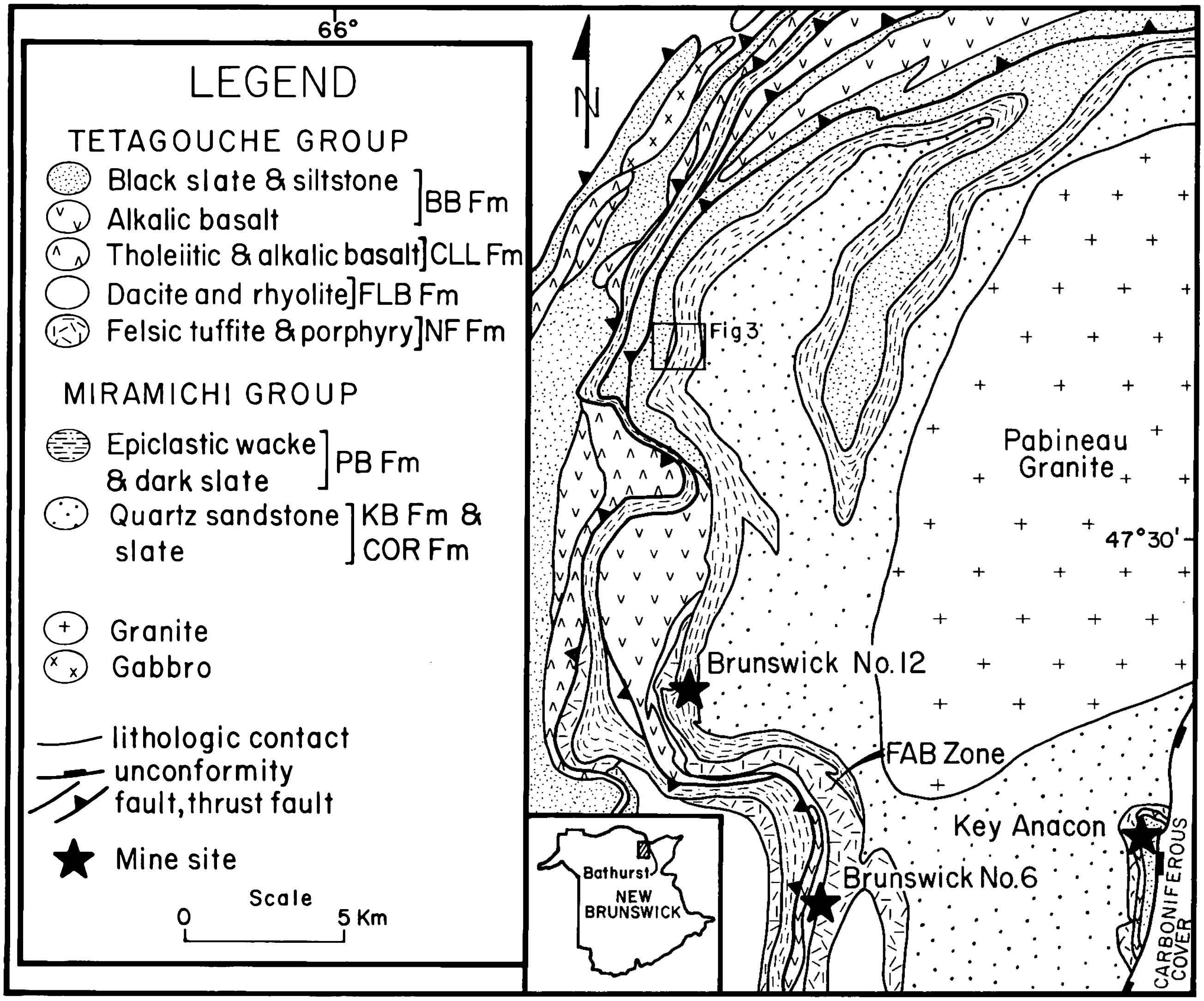

Fig. 1. Geology of the northeastern part of the Bathurst Mining Camp (after van Staal *et al.*, 1991) locating this study area (inset Fig. 3) with respect to the Brunswick and Key Anacon deposits, New Brunswick.

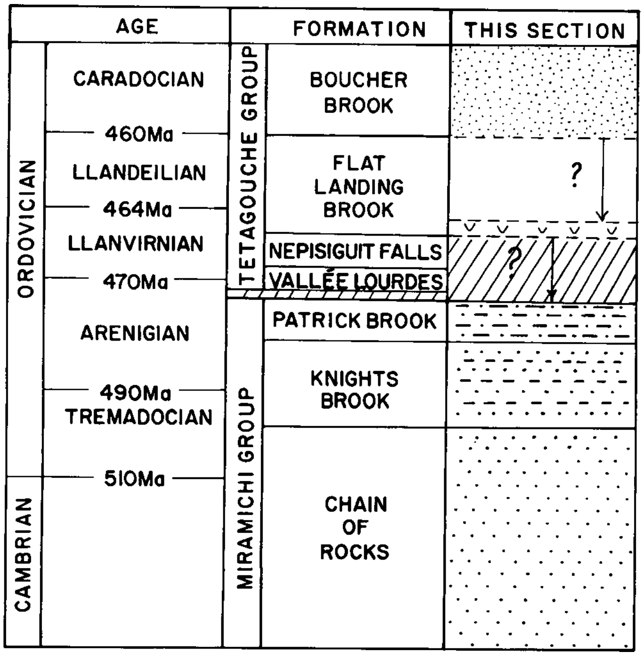

Fig. 2. General stratigraphic column for the Bathurst Mining Camp (modified after Fyffe, 1994) compared with the section examined in this study. The diagonal lines indicate no deposition of the Vallée Lourdes and Nepisiguit Falls formations.

the overlying Nepisiguit Falls Formation (469 ± 2 and 471 ± 3 Ma; van Staal *et al.*, 1992) indicates that the Patrick Brook rocks are late Arenig to early Llanvirnian, like the Vallée Lourdes rocks, as indicated by the paleontological control (Neuman, 1984; van Staal and Fyffe, 1991; Fyffe, 1994).

The drill hole contains dark grey slates and siltstones with lesser proportions of fine grained, light grey sandstones characterized by discrete sedimentological contacts, as well as tectonically disrupted relationships with fragments of siltstone in graphitic slate, which are flattened in the tectonic fabric (Fig. 4a). The upper contact of the Patrick Brook Formation may be locally erosional based on the presence of quartz-rich sandstone pebbles in parts of the overlying Vallée Lourdes Formation, as well as the presence of siltstone clasts in the Nepisiguit Falls Formation at Little Falls on the Tetagouche

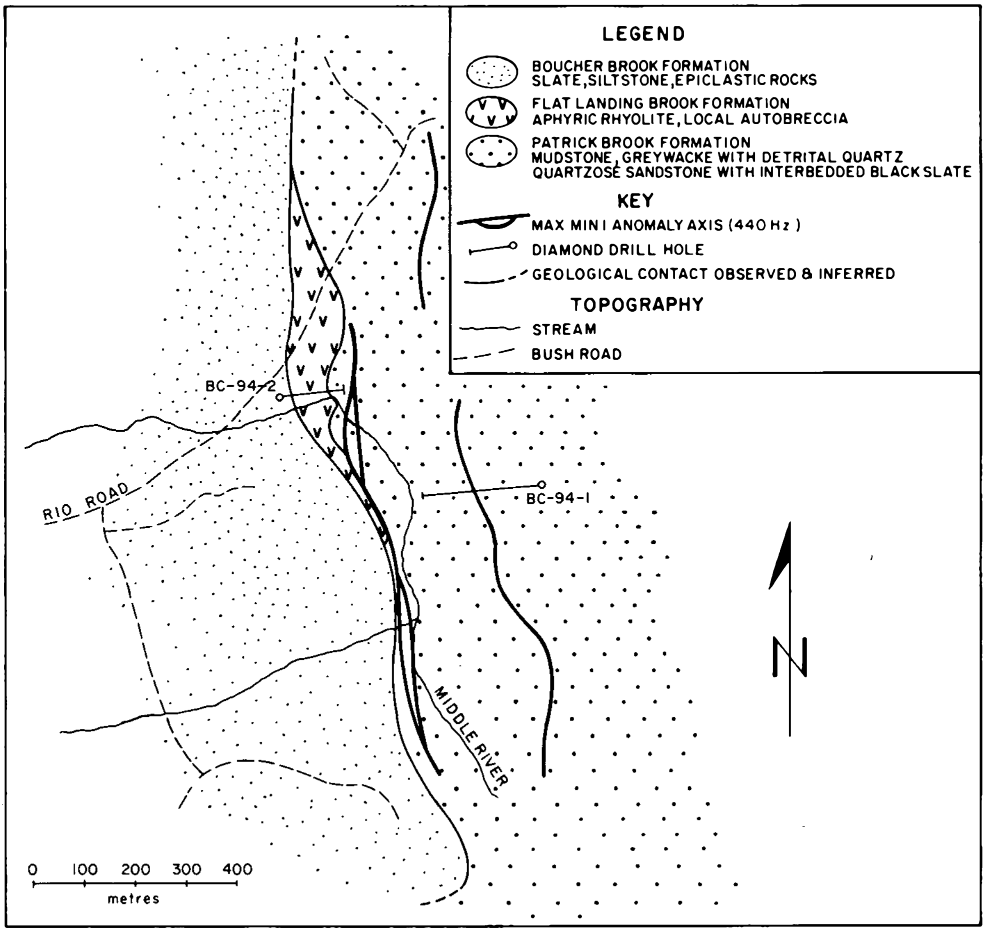

Fig. 3. Local geology of the study area (after Hoy, 1994) with the location of two drill holes and Horizontal Loop Electro-magnetic conductors (HLEM) that are now interpreted to be graphite-rich conductors.

River. However, there is no evidence of a disconformable relationship in the drill hole examined or nearby sections along Middle River, but because of regional considerations is described as a semi-conformable contact.

Boucher Brook Formation (Tetagouche Group)

The Boucher Brook Formation consists of variably coloured, interbedded lithic wacke-siltstone and slates, which overlie the Canoe Landing Lake alkaline basalts and comendites (470 ± 4/2 Ma; Sullivan and van Staal, 1993) and are intercalated with and overlie younger alkaline basalts (457 ± 1 Ma; Beresford suite; van Staal and Sullivan, 1992). The Brunswick alkaline basalts are most closely associated with the rocks of the study area and are interlayered with and are overlain by black, grey, green to red slates and associated cherty equivalents. Conodonts within the upper part of the Brunswick basalt-sediment sequence are early Caradocian (Nowlan, 1981). Skinner (1974) identified mid-Caradocian graptolites from the upper graphitic slates of the Boucher Brook near the mouth of the Tetagouche River, which are, therefore, age-equivalent of the Brunswick basalts.

In the drill hole section, the contact between the black slates and siltstones of the Boucher Brook Formation and underlying rhyolite of the Flat Landing Brook Formation (466 ± 2 Ma; Sullivan and van Staal, 1990) is conformable. The fine- to coarse-grained rhyolite breccia fragments and associated leucocratic hyalotuffaceous rocks (FLB Fm) are mixed with graphitic sedimentary breccia fragments (BB Fm), which decrease in abundance up-section (Fig. 4b). The polymictic breccia is most closely associated with the rhyolite contact and grades into a monomictic breccia and then into thinly interlayered dark grey slates and grey siltstones that are somewhat disrupted tectonically (Fig. 4c).

Depositional setting

Rice and van Staal (1992) suggested that the Patrick Brook Formation represented turbidites deposited on a quiet slope to base of a slope environment, whereas the Boucher Brook rocks were deposited in a deeper starved basin setting (see also Ruitenberg *et al.*, 1977). Van Staal *et al.* (1992) interpreted the Patrick Brook turbidites as representing distal facies equivalents of the Nepisiguit Falls volcaniclastic rocks because of the presence of vitreous quartz crystals in the former. However, Lentz and Goodfellow (1994) have shown that the Patrick Brook rocks are chemically more primitive (i.e., generally higher TiO_2 and Cr) than the Nepisiguit Falls rocks in the FAB zone located between the Brunswick No. 6 and No. 12 deposits on the eastern margin on the Tetagouche

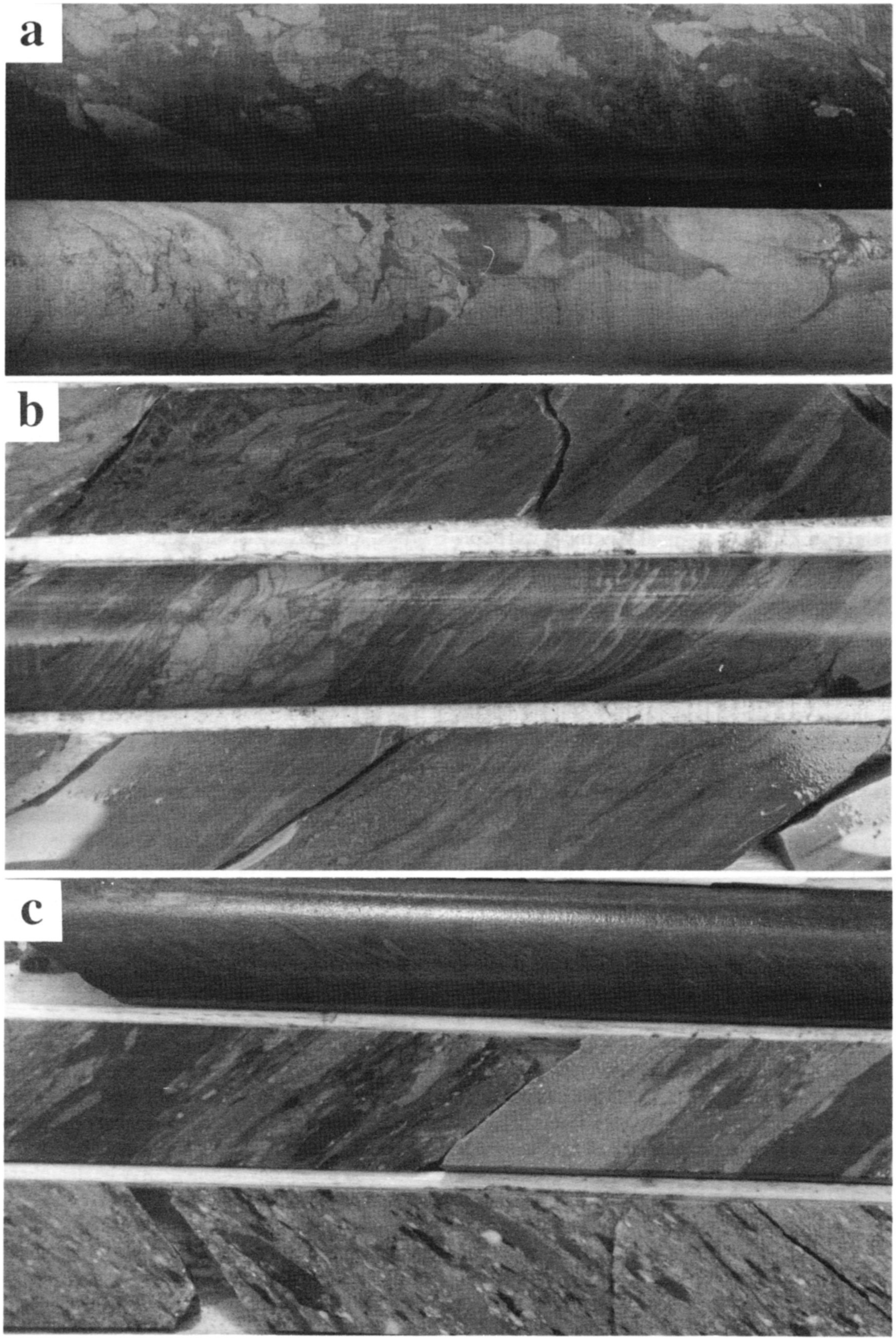

Fig. 4. (a) Quartzose siltstone and graphitic slates with quartz clasts in slate of the Patrick Brook Formation (DDH BC94-2 @ 163.6 to 169.1 m). (b) Carbonaceous and calcareous slate with disrupted sulphide clasts of the Boucher Brook Formation (DDH BC94-2 @ 25 to 31 m). (c) Polymictic breccia (bottom) with pyritic and rhyolitic clasts overlain by siltstone of the Boucher Brook Formation (DDH BC94-2 @ 42.6 to 48.2 m).

Group (Fig. 1). Conglomerates, limestones, and calcareous siltstones of the Vallée Lourdes Formation (middle Arenigian/early Llanvirnian; Fyffe, 1976; Nowlan, 1981; Neuman, 1984) that disconformably overlie the Patrick Brook and possibly Knight's Brook formations (Miramichi Group) at Little Falls on the Tetagouche River (north of the study area) are interpreted as a shallow-water facies sedimentary rocks. Fyffe (1976) and Rice and van Staal (1992) point out that the contact between the Knight's Brook Formation (Miramichi Group) and the Patrick Brook Formation appears conformable. Interestingly, the chemical composition of slates from what is interpreted as Knight's Brook Formation is very similar to slates from the Patrick Brook Formation in the Key Anacon area (Lentz, 1995a). This is supported by the obvious visual similarities between these rocks.

GEOCHEMICAL SYSTEMATICS

Introduction

Eight samples of Boucher Brook sedimentary rocks and nine samples of Patrick Brook sedimentary rocks were collected for major-, trace-, and rare-earth-element (REE) geochemical analysis (see Table 1). The samples were selected from relatively homogeneous and representative segments within each formation (>2 kg); sample intervals are indicated in Table 1. The samples were subdivided into slate (sl), siltstone (slst), and sandstone (sst) because the grain size of sedimentary rocks is a major control on their chemical composition. However, preference was given to the fine grained sedimentary rocks because they are commonly more representative of the source area and depositional environment (cf. Taylor and McLennan, 1985).

Pearson Product correlation coefficients (LeMaitre, 1982) were derived for each of the Boucher Brook and Patrick Brook geochemical data sets (Table 2) in order to identify and quantify mineralogical-element and element-element associations (see Stephens *et al.*, 1975; Vine and Tourtelot, 1970; Argast and Donnelly, 1987; Temple and Walsh, 1994). Pearson Product correlations are based on populations of normal distribution (parametric) and, therefore, should be applicable in most cases. Principal component analysis is commonly used to distil geochemical information from correlation data (Vine and Tourtelot, 1970; Stephens *et al.*, 1975) but was not done because of the low number of samples for the individual data sets. The composition of the quartz-rich Patrick Brook sandstone skews the compositional range of the Patrick Brook samples such that it may affect some element correlations, although, for the most part, it seems only to enhance already strongly positive correlations. Al_2O_3-based variation diagrams (Fig. 5) illustrate significant correlations that are interpreted as variations with respect to the clay components of the rock, which may help to explain the distribution of trace elements and identify significant chemostratigraphic features. As suspected, the predominant trace-element composition is strongly controlled by the proportion of clay (Fig. 6). The raw geochemical data (Fig. 7; Table 1) and certain element ratios (Fig. 8) are plotted in profile to help identify any geochemical discriminants between the two formations, as well as significant trends that may have palaeoenvironmental significance. It is obvious that the Patrick Brook quartz-rich sandstone sample (LPA-515) is chemically distinct from associated interbedded finer grained siltstones and slates; therefore less emphasis is placed on its compositional variation. Ideally, a good chemostratigraphic index should be independent of minor mineralogical and grain size variations or at least allow recognition of instances in which it will not be applicable.

In general, the major-, trace-, and rare-earth-element (REE) composition of these Ordovician slates and siltstones is similar to other post-Archean shales (Gromet *et al.*, 1984; Taylor and McLennan, 1985), as well as other Lower to Upper Ordovician shales from the northeastern Appalachians described by Fyffe and Pickerill (1993) and Lentz *et al.* (1995). As previously mentioned, there are two principal objectives in studying the compositions of fine grained sedimentary rocks; determination of source areas and depositional palaeoenvironment. Goldschmidt (1954) suggested that the geochemical composition of shales (lithogenous components) should represent the upper crust from which they were derived and is the basis for many sediment provenance studies (cf. Taylor and McLennan, 1985). For many high-field-strength (HFS) immobile elements (Al, Ga, Ti, Zr, Hf, REE, Y, and Sc; Taylor and McLennan, 1985; Lentz, 1996), which should include Th, the mechanical and chemical weathering processes do not strongly affect their relative concentrations, although their actual distribution in the weathering products is changed (Goldschmidt, 1954; Fleet, 1984; Taylor and McLennan, 1985) because of their fixation onto and within hydrolysate and Fe-Mn oxidate phases. This is further supported by the high proportion of the LREE in sediment samples that are readily leached without HF digestion of the bulk sample (Roalset, 1975; Fleet, 1984). The mobility of HFSE in diagenetic and early metamorphic processes is determined by their original distribution on clays in sediment and by glass devitrification. However, a very high fluid/rock ratio is still required to mobilize small quantities of HFSE even on the scale of a hand specimen (see Taylor and McLennan, 1985, for a detailed discussion). Although shale samples may represent the overall crustal composition, grain size variations and related mineralogic variations in sedimentary rocks have a major effect on their overall composition (Stephens *et al.*, 1975; Argast and Donnelly, 1987; Temple and Walsh, 1994) that must be evaluated when mineralogic variations are suspected.

The palaeoenvironment may be deciphered by examining some of the components that are mobile in the hydrologic regime. In fine grained sedimentary rocks, these components were deposited both during chemical sedimentation by hydrothermal and hydrogenous processes, and after deposition during diagenesis by subseafloor halmyrolytic processes (Fleet, 1984). The fixation of carbon and sulphur, and the variation in S isotopes can further characterize palaeoenvironmental conditions. The palaeoenvironmental interpretation of the Patrick Brook and Boucher Brook sedimentary rocks is critical in evaluating the seafloor conditions under which massive sulphide deposits of the Bathurst Mining Camp formed.

Geochemical results

From general examination of the overall composition, it is evident that the inverse correlation between SiO_2 and Al_2O_3, and covariation between Na_2O and SiO_2 is indicative of variable proportions of phyllosilicates (chlorite and muscovite) and quartz or albite-quartz mixtures in these sedimentary rocks (Figs. 5, 6a; Table 2). The high negative correlations between major components SiO_2 and Al_2O_3 are a product of the closure problem (Chayes, 1971). The problem of closure can induce (higher) correlations because of an antipathetic relationship between two or more major components (Davis, 1986). In general, the Patrick Brook rocks have high Al_2O_3 compared to the Boucher Brook rocks, except for the quartz-rich sandstone sample. It is well known that higher Al contents relative to other feldspar forming constituents reflect chemical weathering environments, which is why Fritz and Vanko (1992) used a chemical index of alteration (CIA = $Al_2O_3/(Al_2O_3+CaO_{sil}+Na_2O+K_2O)$) in their classification of shales with respect to source areas. In this study, $Al_2O_3/(Al_2O_3+Na_2O+K_2O)$ is used as the chemical weathering index (CWI) because most of the CaO was tied up in carbonate; the CWI's of the Patrick Brook rocks range from 0.77 to 0.87, whereas Boucher Brook rocks range from 0.73 to 0.79 (Fig. 6b). The overall trend suggests that the only difference between these two formations is a higher phyllosilicate content in the Patrick Brook except for the quartz-rich sandstones that are intercalated with them. Therefore, it is unwise to define a discriminant that is strongly a function of mineral percentages because changes in mineral proportions elsewhere in the Bathurst Camp will result in a compositional overlap. Identification of several bimodally distributed elements with little overlap between units is optimal for use in chemostratigraphy.

There is no obvious correlation between grain size (field designation) and chemical composition except for the Patrick Brook quartz-rich sandstone, which causes overlap with the composition of the Boucher Brook rocks. Fe_2O_{3t}, K_2O, TiO_2, La, Yb, Ga, Nb, Th, Be, and Cr (Fig. 5), to name only a few, covary significantly with Al_2O_3 composition in both Boucher Brook and Patrick Brook data, indicating a direct association with the phyllosilicate fraction (see Table 2 for further correlation data). MgO, Na_2O, P_2O_5, and MnO do not significantly covary with Al_2O_3. Zirconium covaries strongly with SiO_2 in the Patrick Brook rocks indicating that zircon is a heavy mineral (cf. Argast and Donnelly, 1987; Crighton and Condie, 1993), whereas no correlation exists in the Boucher Brook rocks. From these data, there seems to be a bimodal distribution for La and Th, to a lesser extent, Yb and Y, which should be significant chemostratigraphically and observable in profile (Figs. 5, 7).

In the chemical profiles (Fig. 7), there is a general trend of decreasing SiO_2 that coincides with increasing TiO_2, Al_2O_3, Fe_2O_{3t}, MgO, CaO, CO_2, and S_t with stratigraphic height in the Boucher Brook rocks. This trend also coincides with increasing Cu, Co, V, Ni, Sc, Cr, Sr, Eu, Yb, and Y. These compositional variations coincide with an increase in the proportion of slate up-section and also indicates a higher mafic component in these sedimentary rocks. The compositions of associated siltstone and sandstone are consistent with the Boucher Brook slate samples. In the Patrick Brook rocks, SiO_2 increases very slightly with a similar magnitude decrease in Al_2O_3 up-section. CaO, CO_2, and Sr also increase slightly with stratigraphic height, whereas Ba, La, Yb, Y, and Th decrease slightly. The major- and trace-element composition of the Patrick Brook rocks is much more uniform than the overlying Boucher Brook rocks indicating a more uniform source for them. In this section, the Patrick Brook rocks have higher TiO_2, K_2O, Ba, Rb, Eu, Be, La, Yb, ΣREE, Y, Ta, Nb, Ga, and Th contents on average than the Boucher Brook rocks, although the TiO_2 contents of the upper section of the Boucher Brook rocks approach those of the Patrick Brook Formation. These variations are consistent with a higher phyllosilicate content (± alkali feldspar) in the Patrick Brook rocks compared to the Boucher Brook rocks and are unlikely to be due to a heavy mineral fraction because the weathering-resistent heavy minerals like zircon correlate strongly with SiO_2. In general, the Boucher Brook rocks have higher MnO, CaO, Na_2O, and CO_2 than the Patrick Brook rocks, which indicates albite, Mn oxyhydroxides, and carbonate in the former. The CO_2 content increases throughout the profile consistent with the occurrence of a limestone unit within Boucher Brook rocks to the northwest. The variation in TiO_2, however, is not solely related to the increasing proportion of phyllosilicate components in the upper part of the Boucher Brook section because the Al/Ti ratios (Fig. 8) are significantly lower compared to the Patrick Brook section, indicating a different source. Hypothetically, the element ratios of related elements should help to distinguish between various source areas for sedimentary rocks as they should behave similarly during weathering, transport, and deposition. In this study, however, related element ratios (i.e., Ti/Sc, etc.) were not very helpful, except for the La/Yb ratio.

The REE patterns for both the Boucher Brook (Fig. 9a) and Patrick Brook (Fig. 9b) rocks are different in LREE/HREE (see La/Yb; Fig. 8), total REE, and Eu contents (Table 1). The La/Yb ratio is not chondrite-normalized because numerous element ratios examined (Fig. 8) are presented as simple element ratios. The significantly higher LREE and weakly higher HREE in the Patrick Brook rocks over the Boucher Brook rocks produces a ratio that may be a reliable chemostratigraphic index providing that the sources of the Boucher Brook rocks do not change. However, Fyffe (1994) found the opposite relationship with slate from near the Boucher Brook type section having a higher ΣREE and LREE/HREE than the Patrick Brook slate that was sampled. Of special note are the differences in the absolute REE contents and LREE/HREE ratios between the sandstones, siltstones, and slates of the Patrick Brook Formation compared to the similar REE contents for equivalent units within the Boucher Brook Formation. The REE variations in the Patrick Brook rocks are characteristic of intense chemical weathering environments (see Balashov *et al.*, 1964; Fleet, 1984) compared to mechanical/physical weathering processes that do not fractionate the rare-earth and other high-field-strength elements.

Table 1. Major and trace-element geochemical data on sedimentary rocks from Diamond Drill Hole BC94-2 in the Middle River area, eastern Bathurst Mining Camp, New Brunswick.

Sample No.	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516				
from (m)	9.5	19.1	29.3	31.4	40.6	48.6	22.6	53	116	119	136	153	169	175	180	192	202				
to (m)	13.5	20	31	37.2	45.2	51.2	23	54	119	125	142	160	174	180	185	196	208				
m	4	0.9	1.7	5.8	4.6	2.6	0.4	1	3	6	6	7	5	5	5	4	6				
Fm	BB	BB	BB	BB	BB	BB	BB	BB	PB	PB	PB	PB	PB	PB	PB	PB	PB	BB		PB	
Unit	sl	sst	sl	slst	slst	slst	sh	slst	sh	slst	slst	slst	sh	sh	sh	sst	sh	$\bar{x}$	1s	$\bar{x}$	1s
SiO_2 wt.%	54.3	60.0	59.7	74.4	70.9	65.8	57.4	71.9	65.5	59.8	65.1	63.2	58.3	57.3	55.8	83.7	58.9	64.3	7.0	63.1	8.0
TiO_2	1.02	1.08	0.50	0.37	0.51	0.64	0.79	0.48	0.93	1.05	1.02	1.04	1.05	1.08	0.98	0.46	0.98	0.67	0.25	0.95	0.18
Al_2O_3	15.60	13.60	12.30	8.30	11.70	14.10	14.60	11.90	16.30	18.50	16.70	18.10	20.90	21.10	18.70	6.30	21.40	12.76	2.12	17.56	4.35
Fe_2O_{3t}	8.60	7.40	8.40	4.60	3.60	4.70	8.30	3.70	5.30	7.20	7.20	7.20	6.90	7.80	8.10	2.80	6.60	6.16	2.07	6.57	1.53
MnO	0.20	0.14	1.04	0.37	0.30	0.23	0.51	0.11	0.08	0.09	0.04	0.03	0.03	0.03	0.04	0.08	0.02	0.36	0.28	0.05	0.03
MgO	2.50	3.32	2.35	1.62	1.42	1.46	3.22	1.46	1.35	1.68	1.72	1.70	1.57	1.88	1.83	0.80	1.64	2.17	0.74	1.57	0.31
CaO	4.08	2.05	2.68	1.80	2.16	1.92	1.39	1.02	1.41	1.18	0.70	0.54	0.26	0.34	0.52	1.54	0.29	2.14	0.87	0.75	0.47
Na_2O	0.30	1.40	0.20	0.60	0.20	0.40	0.70	0.30	0.10	0.30	0.10	0.01	0.10	0.10	0.20	0.10	0.10	0.51	0.38	0.12	0.08
K_2O	3.24	2.48	3.15	1.95	3.15	3.78	3.37	3.26	4.14	4.62	3.73	4.17	5.30	5.07	4.48	0.74	5.33	3.05	0.53	4.18	1.32
H_2O_t	-	2.80	-	-	2.20	2.40	-	2.20	3.30	3.80	4.10	4.40	-	-	-	2.10	-	2.4	0.2	3.5	0.8
CO_2	6.00	5.70	5.60	3.40	3.10	3.70	5.90	2.60	1.50	2.10	0.40	0.30	0.05	0.05	0.20	1.00	0.10	4.5	1.3	0.6	0.7
C	0.40	0.30	0.20	0.10	0.30	0.30	0.60	0.30	0.20	0.20	0.10	0.10	0.80	0.70	3.60	0.20	0.70	0.3	0.1	0.7	1.1
P_2O_5	0.10	0.10	0.17	0.19	0.15	0.14	0.08	0.13	0.10	0.09	0.09	0.09	0.10	0.17	0.12	0.14	0.08	0.13	0.04	0.11	0.03
S_t	2.52	0.90	3.59	1.82	0.42	0.84	2.15	0.41	0.37	0.20	0.11	0.12	1.96	1.51	2.76	0.40	1.14	1.6	1.1	1.0	0.9
Total	98.9	101.3	99.9	99.5	100.1	100.4	99.0	99.8	100.6	100.8	101.1	101.0	97.3	97.1	97.3	100.4	97.3	99.9	0.7	99.2	1.8
LOI	9.1	-	8.2	5	-	-	8.8	-	-	-	-	-	5.5	5.6	8.9	-	4.9	7.8	1.6	6.2	1.6
Ag ppm	0.15	0.15	0.05	0.05	0.1	0.05	0.15	0.05	0.05	0.05	0.16	0.05	0.14	0.15	0.38	0.14	0.13	0.09	0.05	0.14	0.1
Ba	390	250	350	200	350	400	370	310	420	430	440	450	620	590	570	120	660	328	66	478	153
Be	1.7	1.2	2.2	1.5	2	2.3	2.3	2	2.9	3.1	2.4	2.7	3.4	3.4	3.2	0.7	3.5	1.9	0.4	2.8	0.8
Cl	110	178	50	152	146	168	142	175	181	114	142	152	50	183	138	133	149	140	40	138	37
Co	23	19	45	13	8	10	23	7	14	18	16	16	20	19	21	0	17	19	12	16	6
Cr	120	110	24	26	42	58	120	29	53	75	53	59	63	70	78	18	65	66	41	59	17
Cs	11	7.7	9.5	5.9	8.2	9.5	11	8.5	9.2	9.8	7.3	7.5	9.6	7.8	8.8	1.8	7.9	8.9	1.6	7.7	2.3
Cu	47	29	41	17	11	14	46	17	23	33	25	30	42	45	110	5	35	28	14	39	28
F	943	646	1062	703	788	854	834	774	745	666	592	718	813	865	913	255	784	826	123	706	184
Ga	19	15	16	11	15	18	18	16	20	23	21	23	26	28	25	6.3	27	16	2	22	6
Hf	4.2	3.8	4.2	2.6	6.7	5.9	3.4	4.7	6.9	5.3	6.6	6.2	4.3	5.2	5.2	13	4.6	4.4	1.2	6.4	2.5
In	0.06	0.1	0.06	0.12	0.06	0.06	0.05	0.06	0.06	0.08	0.07	0.07	0.09	0.13	0.12	0.05	0.12	0.07	0.02	0.09	0.03
Mo	2.2	0.77	2	1.2	4.5	0.63	4.5	0.8	1.1	0.35	0.22	0.29	6.4	2.5	23	1.4	0.77	2	2	4	7
Nb	12	9.5	15	8.3	15	17	11	15	19	19	18	19	22	23	21	11	21	13	3	19	3
Ni	68	42	39	16	13	18	69	13	27	33	31	31	52	37	69	5	36	35	22	36	16
Pb	19	7.7	39	28	16	15	35	13	12	23	17	16	31	29	52	6.5	30	22	10	24	13
Rb	160	140	170	120	190	200	170	190	230	240	190	200	250	240	220	51	230	168	25	206	58
Sc	23	23	12	7.6	8.5	11	20	8.9	16	19	16	18	20	21	18	4.4	20	14.3	6.2	16.9	4.7
Sr	120	110	110	89	82	91	98	59	100	110	60	44	59	75	66	64	57	95	18	71	20
Ta	0.69	0.57	1	0.48	1.2	1.3	0.66	1	1.2	1.2	0.92	1	1.7	1.7	1.5	0.86	1.6	0.86	0.28	1.3	0.32
Th	8.5	6.4	11	7.1	9.9	12	8.7	9.1	16	16	15	16	17	19	19	12	19	9.1	1.8	16.6	2.2
Tl	1.1	0.94	1.5	0.95	1	1.5	1.1	1.5	1.2	1.2	0.91	1	1.4	1.4	1.6	0.22	1.5	1.2	0.2	1.2	0.4
U	3	2	2.5	3.1	4.1	4.1	3.5	4	4.3	3.6	3.2	5.4	3.6	3.7	8.7	4.7	3.3	3.3	0.7	4.5	1.6
V	160	170	40	33	39	62	130	41	93	110	92	110	130	130	600	12	120	84	55	155	161
Y	27	26	31	27	25	27	24	20	33	35	33	34	30	39	42	30	37	26	3	35	4
Zn	73	79	53	49	53	72	74	63	69	110	85	89	110	140	230	35	99	64	11	107	51
Zr	140	140	140	94	240	210	120	170	250	190	230	210	150	180	180	460	160	157	45	223	89

Table 1. Continued.

Rare-earth-element geochemical data on sedimentary rocks from Diamond Drill Hole BC94-2 in the Middle River area, eastern Bathurst Mining Camp, New Brunswick.

Sample No.	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516				
Fm	BB	BB	BB	BB	BB	BB	BB	BB	PB	PB	PB	PB	PB	PB	PB	PB	PB	BB		PB	
Unit	*sl*	*sst*	*sl*	*slst*	*slst*	*slst*	*sh*	*slst*	*sh*	*slst*	*slst*	*slst*	*sh*	*sh*	*sh*	*sst*	*sh*	x̄	1s	x̄	1s
La	32	23	34	22	31	36	30	28	49	53	48	50	41	57	56	28	55	29	5	49	9
Ce	70	50	90	50	64	73	62	55	97	100	94	96	87	110	100	60	110	64	13	95	14
Pr	7.8	5.4	8.3	5.1	7.6	9	7.4	6.7	12	13	12	12	12	15	14	7.4	14	7.2	1.3	12.4	2.1
Nd	32	23	34	21	30	34	29	26	47	51	47	47	48	57	54	29	55	29	5	48	8
Sm	6.4	4.9	7.2	4.7	6.1	7.1	5.8	5.3	9.2	10	9.3	9.2	9.6	11	11	6.5	11	5.9	0.9	9.6	1.3
Eu	1.4	1.4	1.5	1.1	1.1	1.2	1.2	0.62	1.6	1.8	1.7	1.8	1.7	2.1	2	1.4	1.9	1.2	0.3	1.8	0.2
Gd	5.9	5.2	6.7	5	5.1	5.9	5.1	4.4	7.6	7.9	7.5	7.6	7.4	9.2	8.9	6.3	8.3	5.4	0.7	7.7	0.8
Tb	0.97	0.86	1.1	0.85	0.83	0.95	0.82	0.68	1.2	1.2	1.1	1.2	1.2	1.4	1.4	1	1.4	0.88	0.12	1.23	0.13
Dy	5.1	4.8	5.8	4.8	4.7	5.5	4.8	4	6.8	7.1	6.7	7	6.8	8.1	8	5.8	7.8	4.9	0.5	7.1	0.7
Ho	1	0.97	1.1	0.96	0.97	1.1	1	0.76	1.3	1.4	1.3	1.4	1.4	1.7	1.7	1.2	1.6	0.98	0.1	1.44	0.17
Er	2.8	2.7	3	2.6	2.6	3.1	2.9	2.2	3.8	3.9	3.9	4.1	3.8	4.6	4.9	3.3	4.5	2.7	0.3	4.1	0.5
Tm	0.47	0.48	0.49	0.46	0.45	0.48	0.43	0.33	0.59	0.59	0.59	0.6	0.61	0.72	0.76	0.53	0.69	0.45	0.05	0.63	0.07
Yb	2.8	2.8	2.9	2.5	2.6	3	2.8	2.2	3.7	3.8	3.8	3.9	3.9	4.5	4.8	3.4	4.4	2.7	0.2	4.0	0.4
Lu	0.46	0.45	0.47	0.41	0.42	0.48	0.44	0.33	0.59	0.58	0.59	0.59	0.61	0.68	0.76	0.55	0.67	0.43	0.04	0.62	0.06
ΣREE	168	125	196	121	152	176	150	133	236	249	232	236	237	281	264	150	277	153	25	240	36
La/Yb	10	7.33	9.71	7.50	10.40	10.69	8.67	10.91	12.57	12.37	11.62	11.89	13.59	12.79	11.82	8.28	13.33	9.4	1.3	12.0	1.5
Ce/Ce*	0.99	1.00	1.19	1.05	0.93	0.90	0.93	0.90	0.89	0.85	0.87	0.87	0.87	0.84	0.80	0.93	0.83	0.99	0.10	0.87	0.04
Eu/Eu*	0.26	0.32	0.25	0.26	0.23	0.21	0.26	0.15	0.22	0.23	0.24	0.25	0.23	0.24	0.23	0.25	0.23	0.24	0.05	0.24	0.01

Notes: Sample No. 94-LPA-series; Fm = Formation, BB = Boucher Brook Formation, PB = Patrick Brook Formation; Unit, sl = shale, slst = siltstone, sst = sandstone. The entire sample was crushed and split several times and several hundred grams of the sample was pulverized in a agate swing mill in order to ensure a representative analysis for the interval sampled. All samples were analysed in the geochemical laboratory of the Geological Survey of Canada. Major-elements were determined by X-ray fluorescence spectroscopy on fused disks, ferrous iron was determined by titration with ammonium metavanadate (modified Wilson method), and S, CO_2, and H_2O were determined by infra-red spectrometry of combustibles. Trace elements were analysed by Inductively Coupled Plasma (ICP), emission spectroscopy (ICP-ES) and mass spectroscopy (ICP-MS). The precision of these analyses was determined by comparing duplicate analyses of three internal standards. Based on these comparisons, the precision of major-elements is within 2% and the precision of trace-elements is within 10%, except for H_2O_t (<15%), Ag (<33%), *Hf* (<14%), *In* (<133%), Mo (<20%), Pb (<230%), Sr (<30%), Ta (<24%), and Zn (<13%). The accuracy was determined by comparison of CANMET standards (MRG-1 and SY-2) with accepted values (Abbey, 1979; Govindaraju, 1994). The highest errors are typically associated with the elements of lowest abundance, i.e., near detection limits. A "?" designates uncertainty in the CANMET standard (Abbey, 1979). The relative percent error based on comparison with MRG-1 are: <2% - SiO_2, TiO_2, Al_2O_3, FeO_t, MnO, MgO, CaO, Sr, Zr, Ce?, Pr?, Dy?, Ho?, Er?, and Lu?; <5% - H_2O, CO_2, Co, Hf?, Nb?, Sc?, and Sm?; <15% - K_2O, P_2O_5, S_t, Cr, Cs?, Cu, Pb, Rb, U?, V, Y?, La?, Nd?, Eu?, and Gd?; <25% - Na_2O, Ag?, Ni, Th?, Zn, Tb?, and Yb?; >25% - Ba?, Be?, Mo?, Ta?, and Tm?. The relative percent error based on comparison with SY-2 are: <2% - SiO_2, TiO_2, FeO_t, CaO, K_2O, P_2O_5, Ba, Cs?, Cu, Dy?, Eu, Sr, and Zr; <5% - Al_2O_3, MnO, MgO, CO_2, Ga, Hf?, Lu?, Pb, and Th?; <15% -Na_2O, CO_2, S_t, Be, Cr, Nd?, Pb, Rb, Sc?, Sm?, U, V, Y, and Yb; <25% - H_2O, Er?, La, and Zn; >25% - Ce?, Co, Cr, Mo?, Nb?, Ni, Tb?, and Tm? (see Lentz, 1995b).

Table 2. Pearson Product correlation coefficients (r) for samples from the Boucher Brook Formation (top wedge; n = 8) and the Patrick Brook Formation (bottom wedge; n = 9) from the eastern margin of the Bathurst Mining Camp, New Brunswick.

	Al	Ba	Be	C	Ca	Ce*	Co	CO2	Cr	Cu	Eu	Eu*	F	Fe	Ga	Hf	K	La	Mg	Mn	Na	Nb	Ni	P	Pb	Rb	Sc	Si	Sr	S	Ta	Th	Ti	U	V	Yb	Y	Zn	Zr
Al	1	**0.75**	0.25	**0.77**	0.41	0.46	0.22	0.63	**0.78**	0.59	0.38	0.41	0.36	0.59	**0.94**	0.21	**0.69**	0.54	0.53	-0.13	0.10	0.25	**0.70**	**-0.83**	-0.15	0.40	**0.76**	**-0.84**	0.49	0.13	0.13	0.22	**0.78**	-0.06	**0.73**	0.56	-0.00	**0.83**	0.17
Ba	**0.96**	1	**0.74**	0.59	0.34	0.25	0.18	0.24	0.28	0.32	0.18	-0.01	0.69	0.25	0.90	0.57	**0.94**	**0.93**	-0.01	0.14	-0.53	**0.70**	0.36	-0.39	0.11	**0.78**	0.20	-0.50	0.18	0.16	0.62	**0.74**	0.21	0.42	0.13	0.48	0.08	0.32	0.50
Be	**0.98**	**0.95**	1	0.37	-0.20	0.27	0.15	-0.12	-0.21	0.06	-0.15	-0.37	0.62	-0.05	0.51	0.43	**0.80**	**0.81**	-0.27	0.43	-0.65	**0.73**	-0.01	0.01	0.46	**0.78**	-0.32	-0.06	-0.26	0.16	**0.68**	**0.85**	-0.39	0.62	-0.41	0.21	-0.02	-0.11	0.38
C	0.24	0.38	0.31	1	-0.02	**0.67**	0.02	0.47	**0.76**	0.54	0.04	0.10	0.11	0.43	**0.74**	0.04	0.56	0.29	0.54	-0.13	0.12	0.02	**0.70**	**-0.89**	0.07	0.33	**0.61**	**-0.61**	0.16	0.01	-0.05	0.02	0.55	0.19	0.60	0.23	-0.37	**0.67**	0.03
Ca	**-0.79**	**-0.86**	**-0.69**	-0.34	1	0.02	0.44	0.54	0.33	0.50	**0.68**	0.46	0.53	0.54	0.35	0.04	0.06	0.32	0.19	0.14	-0.22	-0.03	0.48	-0.08	0.06	-0.16	0.45	-0.58	**0.77**	0.53	-0.10	0.04	0.45	-0.38	0.40	0.47	0.60	0.09	-0.05
Ce*	**-0.77**	**-0.80**	**-0.78**	**-0.70**	**0.67**	1	0.62	**0.79**	0.58	**0.82**	0.46	0.43	0.31	**0.80**	0.38	-0.48	0.15	0.11	**0.81**	0.50	0.28	-0.30	**0.82**	-0.54	0.64	-0.15	0.59	-0.72	0.50	0.60	-0.39	-0.09	0.38	-0.38	0.49	0.46	0.19	0.38	-0.51
Co	**0.94**	**0.90**	**0.94**	0.41	**-0.72**	**-0.83**	1	**0.74**	0.10	**0.76**	**0.72**	0.47	**0.71**	**0.81**	0.20	-0.36	0.02	0.27	0.53	**0.85**	-0.05	-0.05	0.55	0.02	**0.70**	-0.20	0.34	-0.65	0.68	0.91	-0.19	0.14	0.16	-0.65	0.17	0.52	0.71	-0.06	-0.44
CO_2	-0.38	-0.54	-0.27	-0.35	**0.84**	0.36	-0.31	1	**0.73**	**0.91**	**0.81**	**0.77**	0.38	**0.98**	0.46	-0.43	0.04	0.11	**0.89**	0.37	0.37	-0.35	**0.92**	-0.55	0.36	-0.32	**0.87**	**-0.95**	**0.90**	**0.69**	-0.46	-0.21	**0.74**	**-0.70**	**0.77**	0.66	0.48	0.53	-0.48
Cr	**0.89**	**0.83**	**0.92**	0.47	-0.61	**-0.90**	**0.95**	-0.15	1	0.63	0.42	0.58	-0.09	0.65	0.57	-0.22	0.15	-0.03	**0.79**	-0.30	0.52	-0.39	**0.84**	**-0.90**	-0.15	-0.16	**0.94**	**-0.78**	0.59	0.10	-0.44	-0.38	**0.92**	-0.31	**0.96**	0.43	-0.07	**0.85**	-0.23
Cu	0.47	0.56	0.52	**0.96**	-0.48	**-0.83**	**0.65**	-0.36	**0.69**	1	0.59	0.45	0.54	**0.96**	0.52	-0.49	0.13	0.17	**0.78**	0.43	0.11	-0.29	**0.95**	-0.53	0.52	-0.23	**0.75**	**-0.90**	**0.73**	**0.79**	-0.46	-0.15	0.56	-0.54	0.63	0.43	0.32	0.39	-0.56
Eu	**0.80**	**0.79**	**0.77**	0.50	**-0.73**	**-0.90**	**0.79**	-0.45	**0.85**	**0.68**	1	**0.90**	0.41	**0.77**	0.21	-0.17	-0.06	0.21	0.58	0.48	0.24	-0.20	0.57	-0.11	0.32	-0.32	0.56	-0.72	**0.95**	0.65	-0.22	0.01	0.51	**-0.69**	0.48	**0.85**	**0.86**	0.21	-0.23
Eu*	-0.51	-0.53	**-0.63**	-0.19	0.07	0.38	-0.54	-0.18	-0.49	-0.26	-0.18	1	0.03	**0.67**	0.14	-0.24	-0.17	-0.04	**0.71**	0.17	0.62	-0.37	0.53	-0.29	0.02	-0.42	**0.69**	-0.66	**0.87**	0.36	-0.35	-0.23	**0.69**	**-0.73**	**0.67**	**0.81**	0.65	0.48	-0.26
F	**0.91**	**0.91**	**0.94**	0.52	**-0.71**	**-0.82**	**0.93**	-0.39	**0.89**	**0.70**	**0.82**	-0.56	1	0.48	0.54	0.16	0.56	**0.80**	-0.01	**0.69**	**-0.67**	0.52	0.35	0.09	0.59	0.38	0.03	-0.49	0.38	**0.73**	0.37	**0.67**	-0.08	-0.01	-0.13	0.44	0.53	-0.15	0.05
Fe	**0.87**	**0.80**	**0.82**	0.41	**-0.74**	**-0.85**	**0.95**	-0.37	**0.92**	**0.65**	**0.86**	-0.30	**0.83**	1	0.46	-0.48	0.06	0.15	**0.85**	0.45	0.26	-0.32	**0.92**	-0.49	0.46	-0.30	**0.80**	**-0.93**	**0.86**	**0.78**	-0.46	-0.16	0.64	**-0.69**	**0.69**	0.60	0.49	0.45	-0.54
Ga	**0.995**	**0.96**	**0.97**	0.30	**-0.81**	**-0.82**	**0.96**	-0.41	**0.91**	0.53	**0.85**	-0.48	**0.93**	**0.90**	1	0.33	**0.86**	**0.74**	0.29	-0.04	-0.21	0.48	0.59	**-0.70**	-0.03	0.61	0.53	**-0.71**	0.30	0.16	0.34	0.46	0.54	0.19	0.48	0.47	-0.05	0.66	0.27
Hf	**-0.985**	**-0.94**	**-0.98**	-0.29	**0.74**	**0.79**	**-0.97**	0.30	**-0.92**	-0.52	**-0.75**	0.58	**-0.91**	**-0.89**	**-0.98**	1	0.63	0.61	-0.52	-0.20	-0.46	**0.82**	-0.43	0.05	-0.43	**0.83**	-0.33	0.20	-0.31	-0.50	**0.90**	0.67	-0.14	0.61	-0.30	0.09	-0.12	-0.05	**0.994**
K	**0.992**	**0.95**	**0.99**	0.22	**-0.73**	**-0.74**	**0.94**	-0.30	**0.89**	0.45	**0.74**	-0.60	**0.91**	**0.83**	**0.98**	**-0.99**	1	**0.89**	-0.12	0.04	-0.48	**0.82**	0.16	-0.38	-0.02	**0.91**	0.06	-0.33	-0.09	-0.05	**0.73**	**0.79**	0.10	0.55	0.01	0.33	-0.14	0.35	0.59
La	**0.81**	**0.74**	**0.83**	0.35	-0.52	**-0.86**	**0.82**	-0.15	**0.89**	0.56	**0.88**	-0.48	**0.82**	**0.84**	**0.85**	**-0.81**	**0.80**	1	-0.21	0.34	-0.66	**0.83**	0.13	-0.06	0.21	**0.79**	-0.06	-0.34	0.13	0.24	**0.76**	**0.92**	-0.04	0.41	-0.15	0.52	0.28	0.08	0.54
Mg	**0.88**	**0.81**	**0.83**	0.35	**-0.74**	**-0.85**	**0.93**	-0.37	**0.91**	0.60	**0.89**	-0.32	**0.83**	**0.99**	**0.91**	**-0.88**	**0.84**	**0.89**	1	0.17	**0.67**	-0.54	**0.83**	**-0.69**	0.19	-0.40	**0.88**	**-0.80**	**0.68**	0.41	-0.61	-0.47	**0.77**	-0.71	**0.83**	0.43	0.17	0.63	-0.53
Mn	-0.62	**-0.72**	-0.49	-0.26	**0.94**	0.51	-0.51	**0.94**	-0.36	-0.35	-0.58	-0.05	-0.55	-0.56	-0.63	0.54	-0.54	-0.38	-0.58	1	-0.30	0.12	0.20	0.37	**0.88**	-0.04	-0.14	-0.25	0.33	**0.79**	0.06	0.37	-0.33	-0.31	-0.31	0.37	0.66	-0.45	-0.26
Na	0.09	0.02	0.19	0.33	0.25	-0.38	0.24	0.58	0.43	0.36	0.18	-0.31	0.09	0.21	0.09	-0.18	0.13	0.25	0.17	0.52	1	**-0.67**	0.24	-0.42	-0.31	-0.56	0.56	-0.21	0.29	-0.19	-0.61	**-0.70**	0.58	-0.60	0.63	0.15	-0.07	0.56	-0.40
Nb	**0.97**	**0.96**	**0.97**	0.34	**-0.78**	**-0.77**	**0.94**	-0.42	**0.88**	0.56	**0.82**	-0.52	**0.96**	**0.85**	**0.98**	**-0.95**	**0.97**	**0.80**	**0.86**	-0.60	0.07	1	-0.36	0.14	-0.11	**0.93**	-0.41	0.10	-0.33	-0.18	**0.97**	**0.92**	-0.31	0.59	-0.46	0.12	-0.03	-0.10	**0.79**
Ni	**0.70**	**0.77**	**0.73**	**0.80**	**-0.67**	**-0.84**	**0.84**	-0.44	**0.81**	**0.91**	**0.68**	-0.43	**0.84**	**0.78**	**0.74**	**-0.76**	**0.70**	0.59	**0.72**	-0.49	0.28	**0.76**	1	**-0.72**	0.35	-0.22	**0.88**	**-0.92**	**0.74**	0.60	-0.49	-0.24	**0.73**	-0.45	**0.80**	0.47	0.20	0.58	-0.48
P	-0.24	-0.19	-0.23	0.20	0.05	0.07	-0.23	-0.19	-0.18	0.13	0.20	0.41	-0.06	-0.14	-0.18	0.33	-0.28	-0.12	-0.12	0.03	-0.05	-0.08	-0.09	1	0.25	-0.15	**-0.83**	**0.68**	-0.28	0.09	0.22	0.24	**-0.82**	0.09	**-0.85**	-0.21	0.39	**-0.89**	0.05
Pb	0.62	**0.73**	**0.65**	**0.88**	**-0.65**	**-0.90**	**0.73**	-0.46	**0.76**	**0.94**	**0.75**	-0.31	**0.76**	**0.70**	**0.67**	**-0.65**	0.60	0.59	**0.65**	-0.48	0.38	**0.68**	**0.94**	0.08	1	-0.17	-0.10	-0.23	0.26	**0.82**	-0.18	0.21	-0.35	-0.16	-0.24	0.24	0.47	-0.41	-0.49
Rb	**0.95**	**0.87**	**0.97**	0.20	-0.58	-0.69	**0.94**	-0.12	**0.90**	0.43	**0.68**	**-0.68**	**0.90**	**0.81**	**0.93**	**-0.96**	**0.97**	**0.80**	**0.81**	-0.36	0.22	**0.94**	**0.68**	-0.29	0.54	1	-0.27	0.04	-0.41	-0.32	**0.91**	**0.82**	-0.17	**0.71**	-0.29	0.06	-0.29	0.10	**0.81**
Sc	**0.992**	**0.92**	**0.98**	0.20	**-0.74**	**-0.76**	**0.95**	-0.30	**0.92**	0.45	**0.80**	-0.51	**0.91**	**0.89**	**0.99**	**-0.98**	**0.99**	**0.84**	**0.90**	-0.54	0.13	**0.96**	**0.68**	-0.24	0.59	**0.96**	1	**-0.88**	**0.73**	0.28	-0.50	-0.42	**0.96**	-0.57	**0.98**	0.46	0.10	**0.81**	-0.35
Si	**-0.96**	**-0.93**	**-0.97**	-0.44	**0.74**	**0.87**	**-0.99**	0.32	**-0.97**	**-0.66**	**-0.85**	0.53	**-0.95**	**-0.93**	**-0.98**	**0.98**	**-0.96**	**-0.86**	**-0.92**	0.53	-0.25	**-0.96**	**-0.83**	0.19	**-0.76**	**-0.94**	**-0.97**	1	**-0.82**	-0.59	0.24	0.01	**-0.79**	0.51	**-0.78**	**-0.68**	-0.36	-0.65	0.27
Sr	-0.02	-0.15	0.13	-0.12	0.57	0.02	0.05	**0.84**	0.20	-0.08	-0.06	-0.49	0.03	-0.06	-0.03	-0.04	0.07	0.19	-0.05	**0.77**	**0.71**	0.02	-0.11	0.04	-0.11	0.25	0.06	-0.07	1	**0.68**	-0.39	-0.15	**0.66**	**-0.72**	**0.66**	**0.77**	**0.74**	0.35	-0.38
S	0.42	0.59	0.47	**0.86**	-0.57	-0.64	0.49	-0.56	0.48	**0.84**	0.54	-0.21	0.62	0.41	0.46	-0.42	0.41	0.27	0.36	-0.46	0.17	0.55	0.82	0.33	**0.89**	0.34	0.36	-0.53	-0.20	1	-0.32	0.09	0.06	-0.53	0.12	0.45	**0.70**	-0.15	-0.59
Ta	**0.75**	**0.84**	**0.79**	0.45	**-0.69**	**-0.65**	**0.66**	-0.47	**0.65**	0.53	**0.68**	-0.42	**0.78**	0.52	**0.76**	**-0.70**	**0.76**	0.49	0.51	-0.52	0.13	**0.82**	**0.68**	0.21	**0.73**	**0.68**	**0.70**	**-0.74**	0.00	**0.78**	1	**0.89**	-0.37	0.65	-0.52	0.12	-0.03	-0.17	**0.89**
Th	**0.88**	**0.93**	**0.90**	0.55	**-0.76**	**-0.90**	**0.84**	-0.48	**0.86**	**0.70**	**0.91**	-0.47	**0.94**	**0.78**	**0.91**	**-0.85**	**0.87**	**0.85**	**0.80**	-0.62	0.12	**0.92**	**0.77**	0.03	**0.81**	**0.80**	**0.86**	**-0.91**	-0.04	**0.67**	**0.85**	1	-0.38	0.53	-0.49	0.36	0.24	-0.17	0.61
Ti	**0.93**	**0.82**	**0.90**	0.12	**-0.66**	**-0.68**	**0.95**	-0.23	**0.88**	0.40	**0.72**	-0.47	**0.84**	**0.92**	**0.93**	**-0.95**	**0.92**	**0.81**	**0.93**	-0.48	0.11	**0.90**	0.64	-0.30	0.48	**0.93**	**0.96**	**-0.92**	0.07	0.21	0.51	**0.72**	1	-0.49	**0.98**	0.46	0.04	**0.87**	-0.15
U	-0.11	-0.02	-0.04	**0.83**	-0.02	-0.38	0.11	-0.16	0.19	**0.76**	0.23	0.11	0.24	0.17	-0.04	0.05	-0.12	0.14	0.10	-0.04	0.14	-0.00	0.51	0.18	0.55	-0.10	-0.10	-0.11	-0.17	0.54	0.01	0.20	-0.11	1	-0.51	-0.32	-0.53	-0.18	0.63
V	0.30	0.40	0.37	**0.97**	-0.33	**-0.75**	0.51	-0.29	0.57	**0.98**	0.54	-0.23	0.58	0.53	0.37	-0.37	0.29	0.46	0.47	-0.24	0.36	0.39	**0.84**	0.09	**0.87**	0.29	0.29	-0.51	-0.08	**0.77**	0.37	0.56	0.25	**0.86**	1	0.39	0.00	**0.85**	-0.30
Yb	**0.67**	**0.76**	**0.68**	**0.76**	**-0.71**	**-0.93**	**0.69**	-0.56	**0.74**	**0.84**	**0.91**	-0.24	**0.79**	**0.72**	**0.73**	-0.63	0.62	**0.76**	**0.73**	-0.62	0.15	**0.73**	**0.78**	0.21	**0.89**	0.53	**0.63**	**-0.75**	-0.18	**0.77**	**0.72**	**0.91**	0.51	0.46	**0.76**	1	**0.72**	0.40	0.04
Y	0.50	0.53	0.53	**0.71**	-0.42	**-0.88**	0.56	-0.27	**0.70**	**0.79**	**0.87**	-0.20	**0.66**	**0.65**	0.57	-0.48	0.46	**0.81**	**0.67**	-0.33	0.32	0.55	0.61	0.24	**0.76**	0.42	0.50	**-0.63**	0.06	0.55	0.47	**0.78**	0.42	0.53	**0.75**	**0.91**	1	-0.22	-0.19
Zn	0.55	0.61	0.59	**0.90**	-0.54	**-0.89**	**0.72**	-0.35	**0.78**	**0.98**	**0.79**	-0.24	**0.75**	**0.75**	0.62	-0.59	0.53	0.65	**0.70**	-0.37	0.41	**0.64**	**0.91**	0.19	**0.95**	0.51	0.55	**-0.73**	-0.02	**0.81**	0.59	**0.75**	0.50	**0.66**	**0.93**	**0.88**	**0.84**	1	-0.04
Zr	**-0.99**	**-0.94**	**-0.97**	-0.29	**0.76**	**0.79**	**-0.98**	0.33	**-0.92**	-0.52	**-0.76**	0.55	**-0.91**	**-0.90**	**-0.98**	**0.999**	**-0.98**	**-0.81**	**-0.90**	0.57	-0.16	**-0.95**	**-0.77**	0.33	**-0.68**	**-0.95**	**-0.99**	**0.98**	-0.00	-0.42	**-0.70**	**-0.85**	**-0.95**	0.04	-0.37	**-0.65**	-0.49	-0.59	1

Notes: Bold >95% confidence level which is r = 0.63 for Patrick Brook rocks and r = 0.67 for Boucher Brook rocks if they are normally distributed (LeMaitre, 1982).

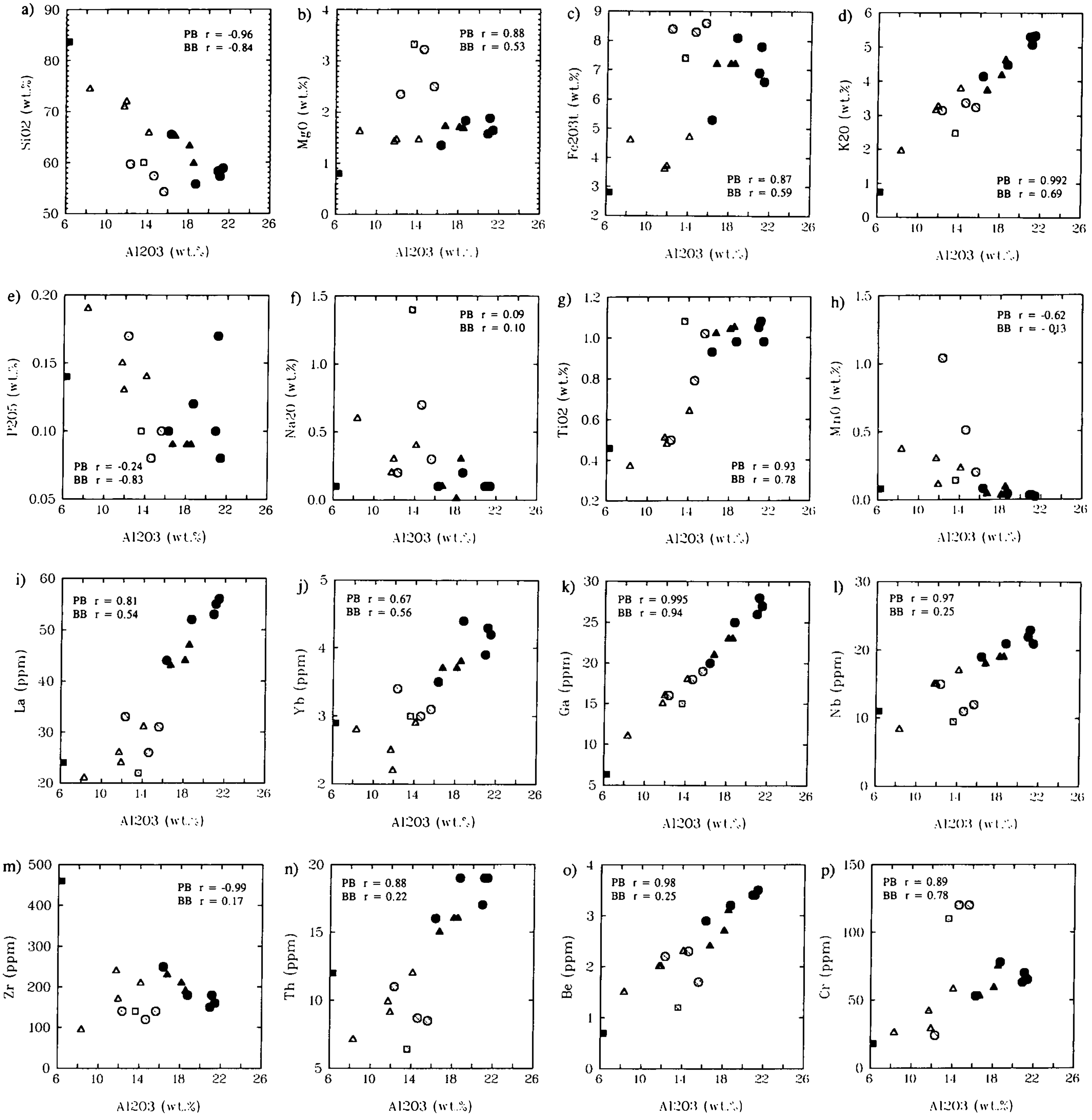

Fig. 5. Al_2O_3-based variation diagrams illustrating the major-, trace-, and rare-earth-element (Table 1) variations in Patrick Brook (PB) slates (●), siltstones (▲), and sandstone (■) and Boucher Brook (BB) slates (○), siltstones (△), and sandstone (□) for many geologically significant mineral-element correlations. Pearson Product correlation coefficients (r) are presented for each formation (see Table 2).

This difference in REE abundances in the slates and sandstones of the Patrick Brook was also noted in the Key Anacon area (Lentz, 1995a).

The Ce anomaly (Ce/Ce*) and Eu anomaly (Eu/Eu*) were calculated by interpolation (see Henderson, 1984). The highest positive Ce anomaly (Ce/Ce* = 1.19; LPA-502) is coincident with the highest MnO contents consistent with hydrogenous precipitation in the Boucher Brook rocks (see Piper, 1974; Fleet, 1984). The negative cerium anomaly in the Patrick Brook rocks is related to the phyllosilicate fraction and Ce/Ce* correlates inversely with Fe_2O_{3t} (Fig. 10a) and positively with SiO_2 (Fig. 10b) consistent with extreme chemical weathering (see Nesbitt, 1979; Fleet, 1984). The Ce/Ce* in these rocks covaries significantly with Ni, Cu, Fe, Mg, and CO_2 and is less pronounced with Mn. Ce/Ce* and inversely correlative with Fe/Mn, which is also a good

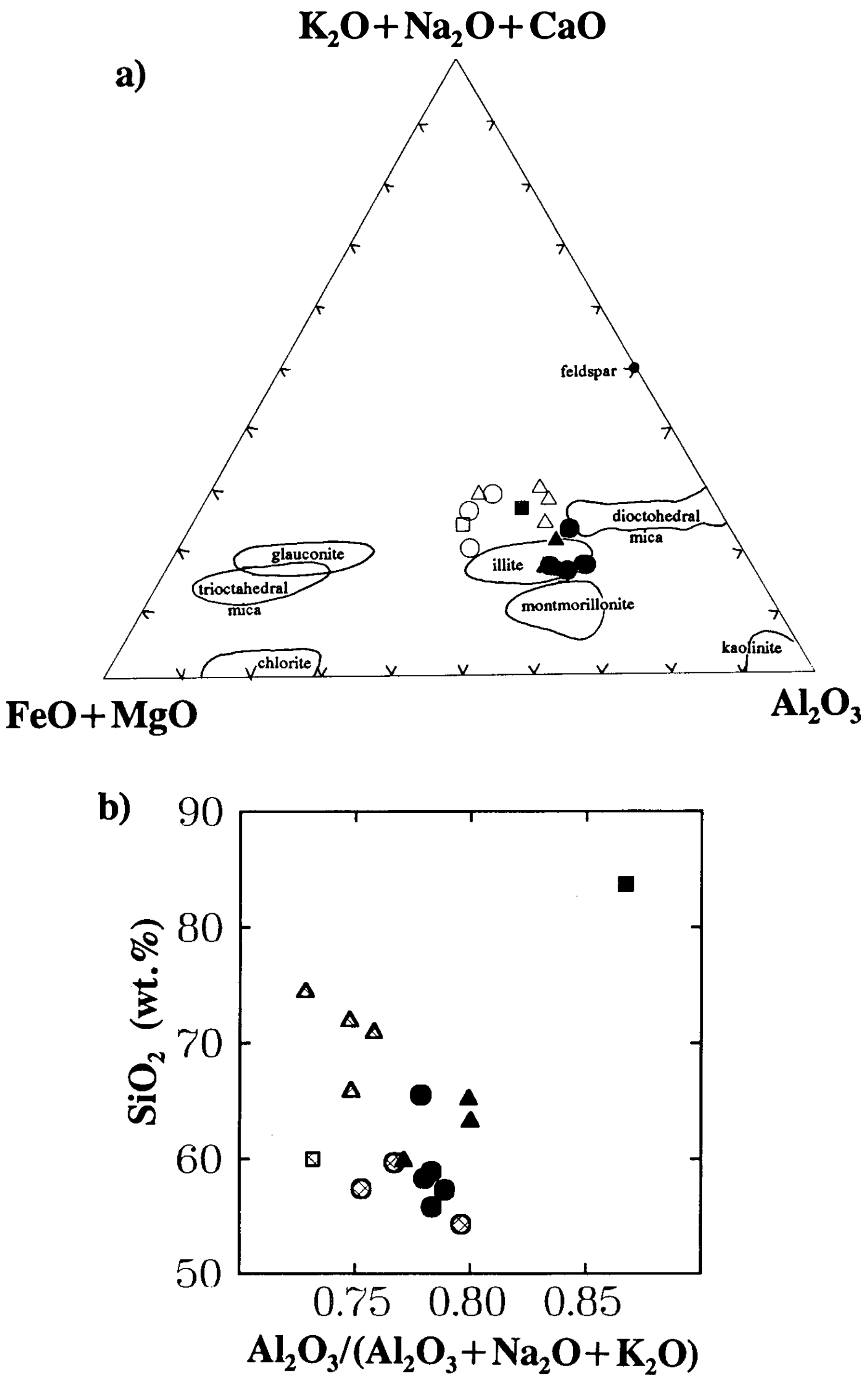

Fig. 6. (a) Ternary molecular (FeO_t+MgO) - (K_2O+Na_2O+CaO) - Al_2O_3 plot illustrating the distribution of Patrick Brook and Boucher Brook rocks relative to common sedimentary minerals (see Goodfellow *et al.*, 1980). (b) SiO_2 versus Al_2O_3/(Al_2O_3+Na_2O+K_2O) molar ratio. See Figure 5 for symbols.

redox index (Fig. 11). The normal Ce contents in the Boucher Brook rocks could have formed by low Ce (negative anomalies) enhanced by hydrogenous precipitation or represent very immature or volcanogenic sediments (lithogenous) formed and deposited in a submarine environment. The Patrick Brook rocks have a consistently negative Ce anomaly (Ce/Ce* = 0.87) compared to the Boucher Brook rocks (Ce/Ce* = 0.98).

The Eu anomalies are quite pronounced and of equal magnitude in both formations, which could be characteristic of the source or breakdown of feldspar, which may be associated with weathering or even seafloor processes. In the Boucher Brook rocks, Eu/Eu* correlates with both CO_2 and Sr (Fig. 10c, d), which also covary with the mafic phyllosilicate fraction (K, Al, Fe and Mg), possibly indicating a mafic derivation and redistribution into carbonates during diagenesis.

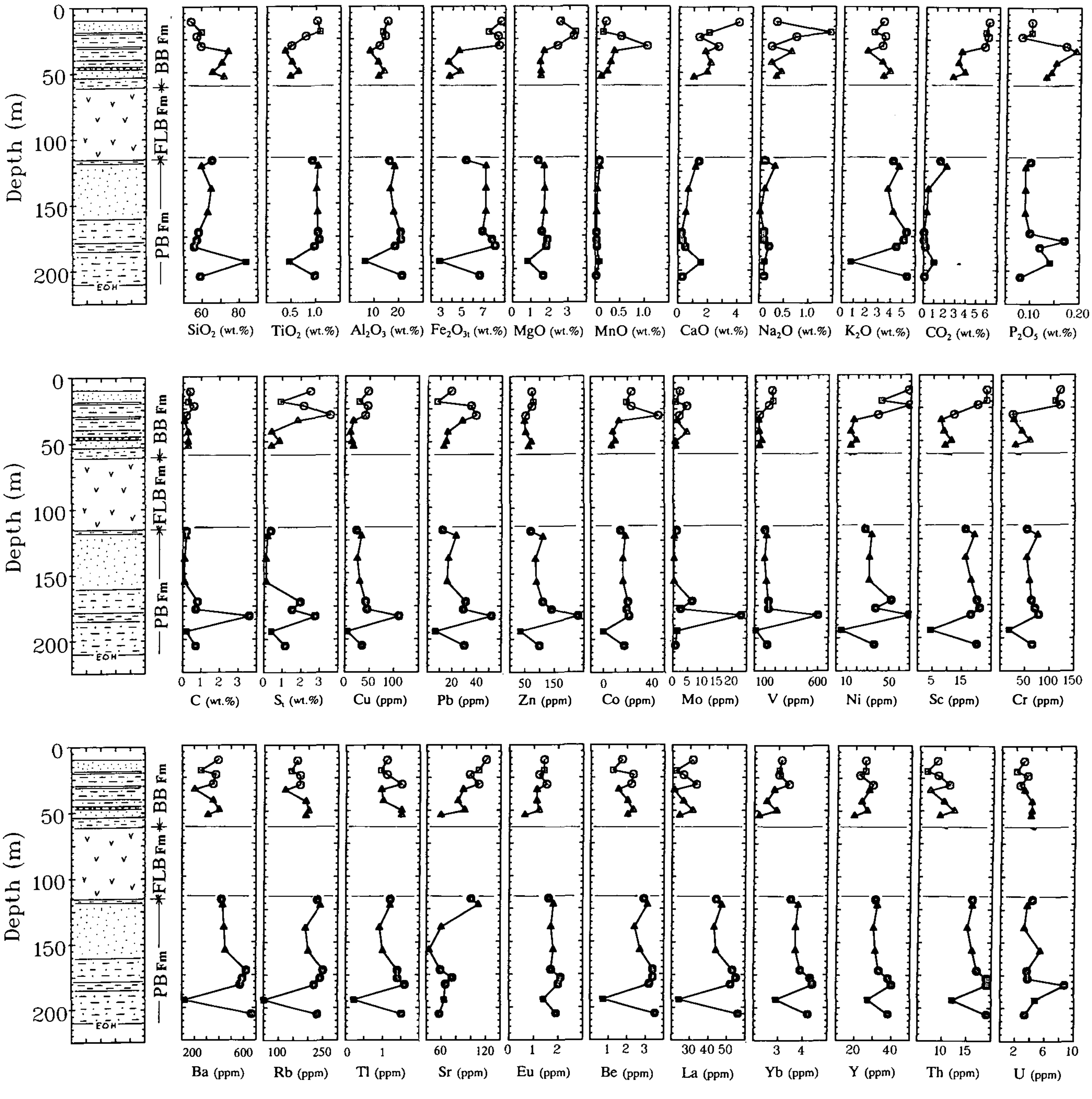

Fig. 7. Major-, trace-, and rare-earth-element data profiled down hole to illustrate potential chemostratigraphic variations and elemental-mineralogical variation that may be significant in paleoenvironmental interpretation. See Figure 5 for symbols. The symbology in the stratigraphic profiles is dashes = slates, dots and dashes = siltstones, and dots = sandstones; v = rhyolite.

Sulphur isotopic considerations

The sulphur isotopic compositions were determined on pyrite-rich separates and powdered samples with S analyses (Table 3). The powdered samples were determined by KIBA whereas the pyrite separates were prepared by combustion with Cu_2O (see Table 3) and trapped as pure SO_2 gas. The sulphur isotopes were measured on the evolved SO_2 gas with a VG micromass 602 mass spectrometer at the Ottawa-Carleton Geoscience Centre Isotope Facility by Gilles St. Jean. The precision (2σ) of $\delta^{34}S$ is less than 0.2‰. The results are standardized relative to the Cañon Diable Troilite using McMaster University reference standards (Rees, 1978).

The sulphide separates were pyrite-rich fragments/clasts that occurred within shale, whereas the remaining pyrite occurred as concretions or euhedral crystals. The $\delta^{34}S$ of clastic pyrite ranged from approximately 13 to 28‰, which is similar to the range of other massive sulphide deposits in the Bathurst Camp (Fig. 12; Tupper, 1960; DeChow, 1960; Lusk and Crocket, 1969; Goodfellow and Peter, 1996). These values with the higher Fe/Mn (>20) support a very reducing environment coincident with massive sulphide formation resulting from a high proportion (50 to 100%) of SO_4^{2-}

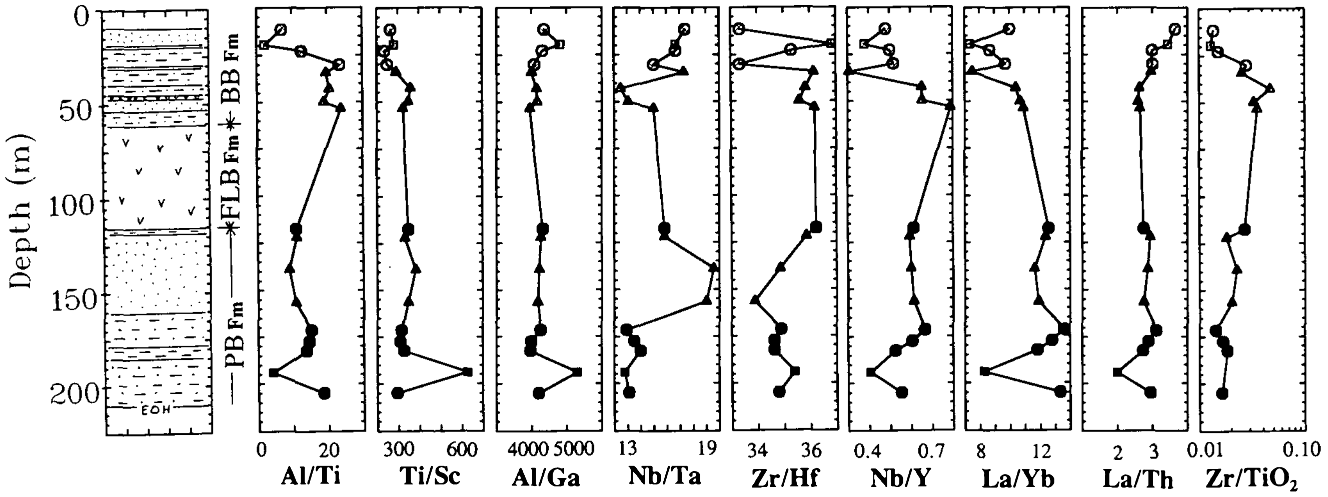

Fig. 8. Element ratios profiled down hole to illustrate potential chemostratigraphic variations and elemental-mineralogical variation that may be significant in paleoenvironmental interpretation. See Figure 5 for symbols. The symbology in the stratigraphic profiles is dashes - slates, dots and dashes = siltstones, and dots = sandstones; v = rhyolite.

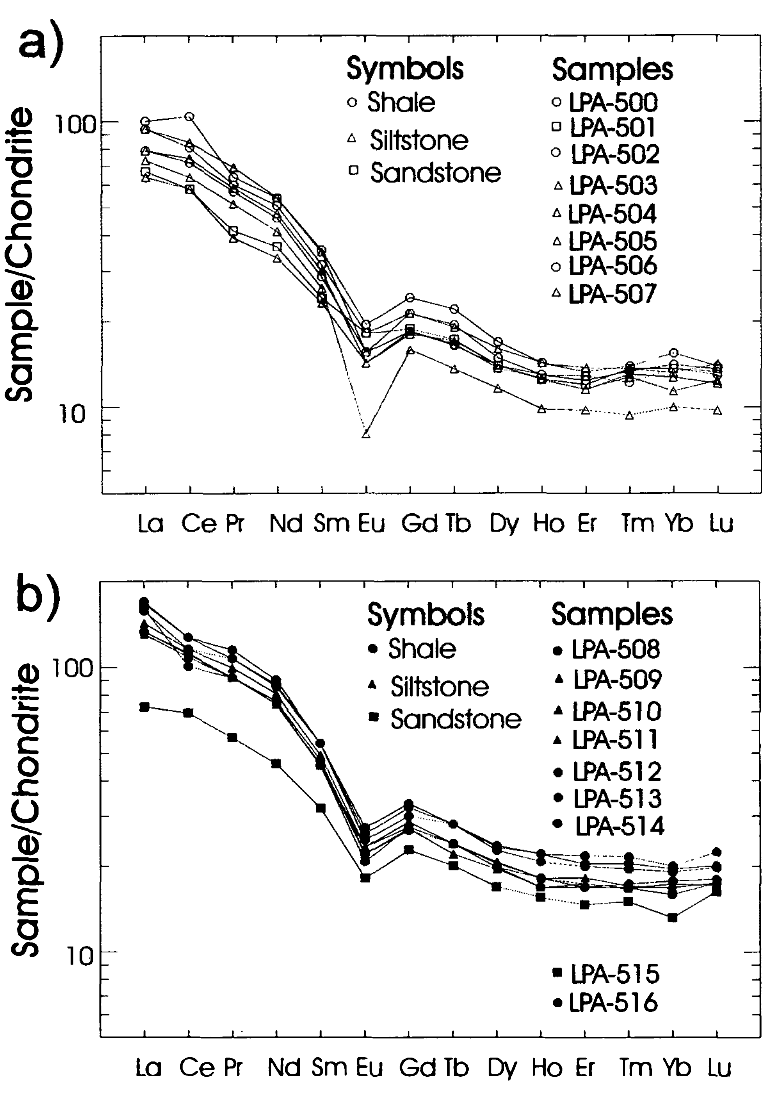

Fig. 9. Chondrite-normalized (Anders and Ebihara, 1982) rare-earth-element profiles for (a) Boucher Brook rocks, and (b) Patrick Brook rocks.

reduced to H_2S in a stratified ocean. Interestingly, the Patrick Brook rocks have a range of $\delta^{34}S$ values from 0.4 to 7.3‰, which is much lower than the inferred $\delta^{34}S$ composition of Patrick Brook sedimentary rocks from the Brunswick deposit ($\delta^{34}S = 19.1 \pm 3.8$‰; Goodfellow and Peter, 1996), as well as those from the stringer sulphide stockwork zone (Lentz and Goodfellow, 1993; Peter and Goodfellow, 1993; Goodfellow and Peter, 1996). This is probably due to a contribution of biogenically-reduced sulphur to the total sulphur in the sequence. Alternatively, the lighter $\delta^{34}S$ in these Patrick Brook rocks could reflect a lower proportion of reduced seawater sulphate (i.e., low SO_4^{2-}/H_2S; Goodfellow and Jonasson, 1984) compared to the Brunswick area (Fig. 1) because these rocks (PB Fm) are higher up within the anoxic water column (i.e., shallower). This latter hypothesis is supported by the lower proportion of volcanic rocks in this part of the sequence compared to the Brunswick area.

The uppermost samples of the Boucher Brook Formation decrease from -6.5 to -17.3‰ with stratigraphic height indicating an increase in biogenic sulphur or possibly a minor component of reduced seawater sulphate by Rayleigh fractionation. The change in sulphur isotopic composition is coincident with higher Mn content compared to the Patrick Brook rocks, which probably reflects local disruption of the anoxic environment.

DISCUSSION

Sediment provenance

The Miramichi Group is comprised of three formations; Chain of Rocks, Knight's Brook, and Patrick Brook formations (van Staal and Fyffe, 1991; Langton and McCutcheon, 1993; Steve McCutcheon and Les Fyffe, personal communication). The lower sequence (Chain of Rocks) is dominated by greenish quartzose sandstones with lesser proportions of grey-green siltstones and shales and is gradational

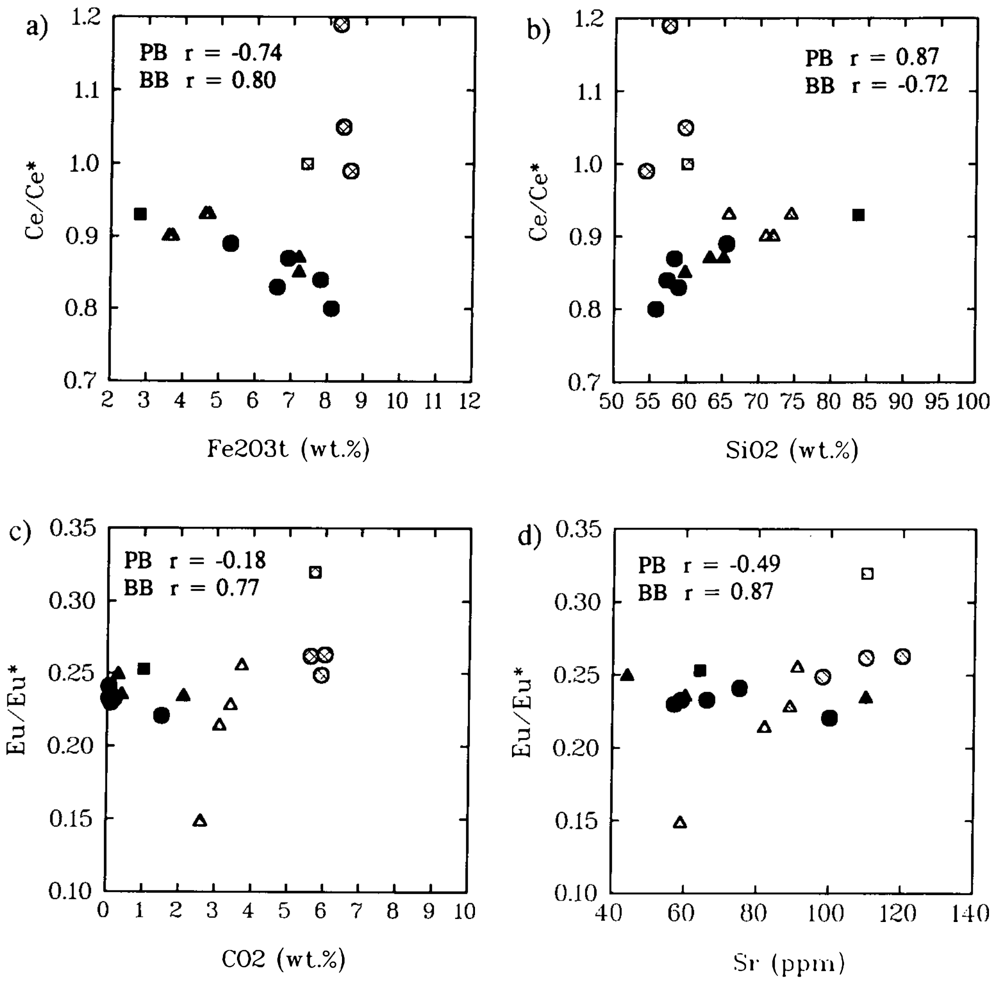

Fig. 10. (a) Ce/Ce* versus Fe_2O_{3t} and (b) Ce/Ce* versus SiO_2 illustrating that the negative Ce anomaly (Ce/Ce*) is greater within the phyllosilicate-rich fractions of the Patrick Brook Formation and that there is a weak positive Ce anomaly in the Boucher Brook Formation. The Ce anomaly was calculated according to McLennan (1989). (c) Eu/Eu* versus CO_2 and (d) Eu/Eu* versus Sr illustrating that the Eu anomaly in the Boucher Brook rocks is moderately correlative with CO_2 and strongly correlative with Sr (see Table 2). See Figure 5 for symbols.

with the Knight's Brook Formation that is dominated by quartzose grey-green siltstone and shales. In most areas of the Bathurst Camp, the contact of Patrick Brook Formation with the Knight's Brook Formation is also gradational. The Miramichi Group is considered to lie within the Gander Zone, whereas the Tetagouche Group is considered part of the Dunnage Zone based on the maturity of the sedimentary rocks, lithologic associations, and provenance studies (see Rast *et al.*, 1976; Williams, 1979; van Staal and Fyffe, 1991). In the past, rocks of the Patrick Brook Formation were included in the Miramichi Group but then were reinterpreted as representing part of the basal Tetagouche Group because of the presence of volcanic quartz phenoclasts in the sandtones and siltstones and stratigraphic relationships (van Staal *et al.*, 1992). More recently, these stratigraphic relationships

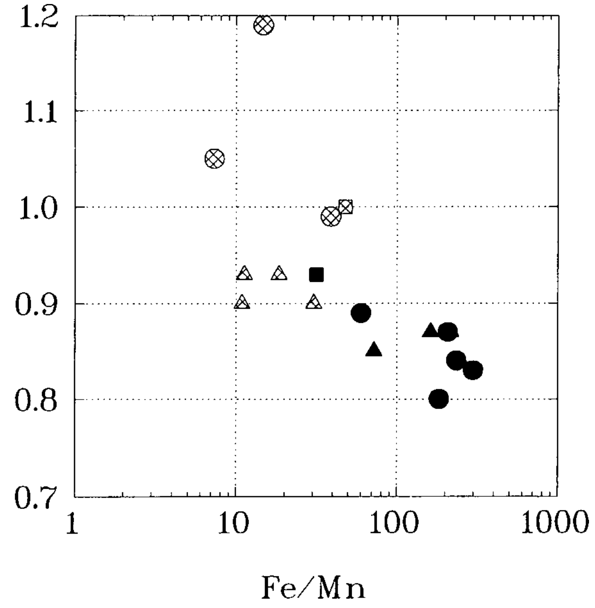

Fig. 11. Fe/Mn versus Ce/Ce* illustrating strong negative correlation. The Ce anomaly was calculated according to McLennan (1989). See Figure 5 for symbols.

Table 3. Sulphur isotope analyses and sample descriptions from Boucher Brook and Patrick Brook formation graphitic sedimentary rocks, DDH BC94-2, Bathurst Mining Camp, New Brunswick.

Sample		S_t wt. %	$\delta^{34}S_{CDT}$ (‰)	Description
LPA-500	Pwdr	2.52	-17.3	homogeneous black shale/siltstone with <1% pyrite
LPA-501	Pwdr	0.90	-16.8	homogeneous greywacke/sandstone with clastic pyrite
LPA-502	Pwdr	3.59	21.8	light grey pyritic chert/shale/siltstone (heterogeneous), exhalative sulphide layers
LPA-503	Py	1.82	22.6	grey to black siltsone with very minor pyrite concretions and a few quartzite interlayers and very minor free graphite
LPA-504	Py	0.42	13.4	finely laminated light to dark grey siltstones with <1% pyrite
LPA-505	Py	0.84	27.6	weakly layered medium grey siltstone with minor concretionary pyrite
LPA-506	Py	2.15	-6.5	graphitic shale with minor quartzose siltstones (<10%) and a few pyritic layers(?)
LPA-507	Pwdr	0.41	16.9	light to medium grey siltstone/greywacke with minor clastic? pyrite above hyalotuff units
LPA-508	Py	0.37	2.8	graphitic shale with pyrite layers and concretions just below sericitic rhyolite (FLB Fm)
LPA-509	-			homogeneous medium grey siltstone
LPA-510	-			very homogeneous light to medium grey siltstone
LPA-511	-			mixed medium grey siltstone and quartzitic siltstone interlayers that are boudinaged
LPA-512	Pwdr	1.96	5.7	graphitic shale with a few fragments (<5%)
LPA-513	Pwdr	1.51	7.3	very graphite rich shale
LPA-514	Pwdr	2.76	0.4	very graphitic shale with few pyrite concretions
LPA-515	-			very homogeneous, medium to light grey siltstone/sandstone
LPA-516	Pwdr	1.14	5.4	medium to dark grey siltstone/shale

Notes: Pyrite separates were approximately 80% pure with quartz gangue. The sulphur in the powders (Pwdr) were extracted by KIBA method. CDT = Canyon Diablo Troilite standard.

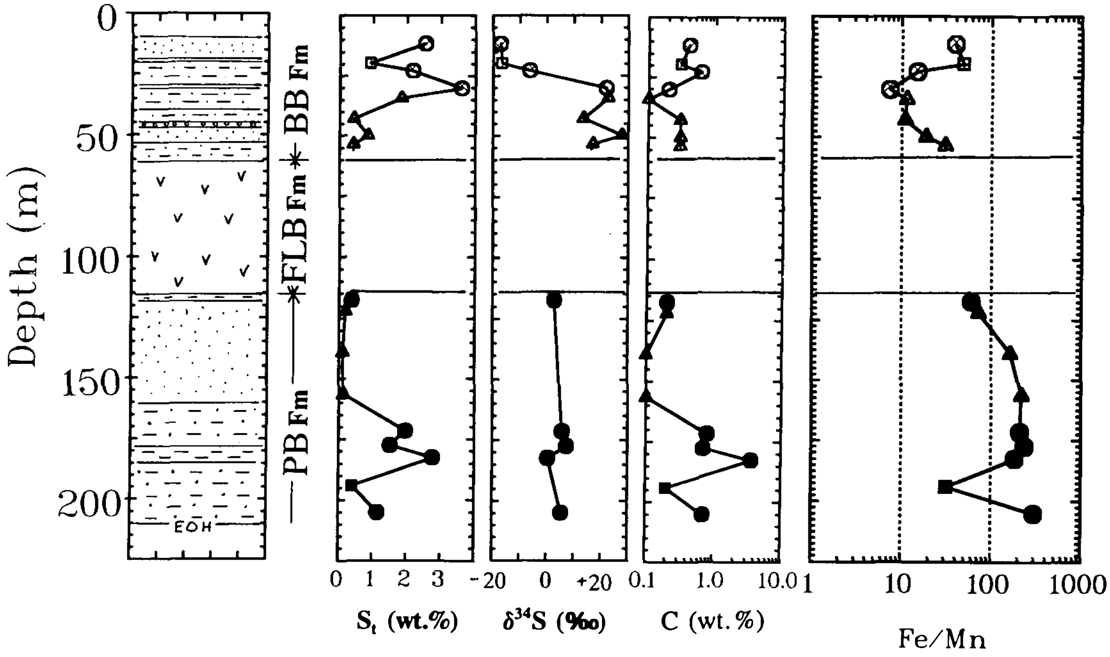

Fig. 12. S (wt. %), $\delta^{34}S$ (‰), C (wt. %), and Fe/Mn profiled down hole to illustrate variations that may be significant in paleoenvironmental interpretation. See Figure 5 for symbols. The symbology in the stratigraphic profiles is dashes = slates, dots and dashes = siltstones, and dots = sandstones; v = rhyolite.

have been re-examined in the type area and show that the Patrick Brook Formation underlies the Vallée Lourdes Formation conglomeratic rocks that marks the Miramichi-Tetagouche Group (Les Fyffe and Steve McCutcheon, personal communication; see Fig. 2).

The discontinuous monolithic breccias (sedimentary melangé), as well as broken formations (tectonic mélange) developed locally in the upper part of the Patrick Brook rocks supports the interpretation that these rocks belong in the Miramichi Group because of their regional significance. The breccias/conglomerates in the Patrick Brook and overlying Vallée Lourdes formations indicate local and/or regional? faulting and debris sedimentation related to opening of the back-arc and related volcanism in the area, although lithospheric doming and exhumation (see van Staal and Fyffe, 1991; van Staal *et al.*, 1996) as a result of ophiolite obduction or mantle upwelling may also be responsible (van Staal *et al.*, 1991, 1996). Also, quartz phenoclasts are not entirely unique to the Patrick Brook rocks, having also been identified within the lower Miramichi Group sequence (Langton and McCutcheon, 1993). Elsewhere along the Brunswick Belt, the Nepisiguit Falls Formation, a felsic volcanic and volcaniclastic sequence, usually overlies the Patrick Brook sedimentary rocks. Generally, this contact is sharp, although in several parts of the Bathurst Camp, the contact is infingered and gradational (i.e., Key Anacon). Although preliminary, the chemical similarity of the Knights Brook and Patrick Brook formations (Lentz, 1995a) suggests that there is a compositional continuum between the sedimentary rocks of the middle to upper Miramichi Group.

This section from the Patrick Brook Formation (Miramichi Group) to the Boucher Brook Formation (Tetagouche Group) represents a unique locality in which to study the change in sedimentological provenance and geotectonic changes across the Gander-Dunnage boundary. In northern New Brunswick, the Miramichi-Tetagouche contact (Gander-Dunnage boundary) is considered disconformable in contrast to the allochthonous relationship along much of this boundary in north and central Newfoundland (Colman-Sadd *et al.*, 1992; Piasecki, 1992), although, as in New Brunswick, rocks of the Dunnage Zone (Indian Bay Big Pond Formation) occurring within the Gander Zone proper (see Wonderly and Neuman, 1984) may have a strained, autochthonous (unconformable) contact (see van Staal and Williams, 1991).

A general comparison of the key discriminating elements (LREE, HREE, Eu, Y, Ta, Nb, Ga, and Th) from Appalachian shales presented by Fyffe and Pickerill (1993) with those of this study indicates that the Patrick Brook rocks are most similar to shales associated with both the Gander and Avalon margins, whereas the Boucher Brook rocks are similar to shales of the Laurentian margin and Gander Zone. The chemical similarity of the Patrick Brook rocks to shales of the Gander Zone and the Avalon margin is consistent with a peri-Gondwanan source area (see O'Brien *et al.*, 1983). The Pan-African age for zircon (610 to 680 Ma) from the Miramichi Group in south-central New Brunswick (David *et al.*, 1991) and the southerly palaeomagnetic latitudes determined on alkaline mafic rocks from the overlying Tetagouche Group (Liss *et al.*, 1994) adds further support to this, although the 40°S latitude determined indicates that there must have been considerable sedimentary transport from the source area if indeed the sediments were from an area of intense chemical weathering (i.e., more equatorial). As previously alluded to, the general absence of feldspar in rocks of the Miramichi Group is consistent with an environment of intense chemical weathering. The high REE, La/Yb, Eu, Nb, Ta, Ga, and Th in the Patrick Brook rocks is also compatible with a derivation from an upper crustal source. The similarity of the Boucher Brook slates to those shales derived from the Laurentian margin might support a change in source area as is the interpretation for shales of the Humber Zone (Fyffe and Pickerill, 1993). More likely, weathering and erosion of juvenile arc (Popelogan arc - northwest; van Staal and Fyffe, 1991) and/or immediately associated back-arc Tetagouche felsic to alkaline mafic volcanic material (van Staal, 1987; van Staal *et al.*, 1991) coincident with either the submergence of the eroding peri-Gondwanan margin or increased juvenile volcanic sedimentation could explain the observed compositional differences. This is supported by data presented for various sedimentary rocks in the Miramichi Terrane (Connell and Hattie, 1990), which indicate that the Boucher Brook sedimentary rocks have a variable mafic component suggesting that some components were probably locally derived (Lentz *et al.*, 1995).

Considering the divergent observations of Fyffe (1994) for a relatively small sample population, the large area of these rocks, and diversity of probable source areas for Boucher Brook sedimentation, it may be difficult to find generally applicable HFSE chemostratigraphic indices to discriminate between the Boucher Brook and Patrick Brook formations throughout the Bathurst Camp. In general, however, Patrick Brook rocks seem to be more mature mineralogically, i.e., generally devoid of feldspars or volcanic rock fragments indicative of chemical weathering in their source areas, which affects both the mobile and immobile chemical systematics. On the other hand, sediments of the Boucher Brook Formation, which seem to have been derived locally, may retain some compositional signatures of their source area and could indicate volcanogenic affinities within the section.

Analogous to the Miramichi Group, sedimentary rocks of the Gander Zone in Newfoundland received detrital material from eroding Avalon zone rocks (O'Brien *et al.*, 1983), which is supported by U/Pb geochronological evidence (Colman-Sadd *et al.*, 1992). The recognized disconformity between the Miramichi and Tetagouche groups is hypothesized to represent the Penobscot Orogeny (disturbance) in related rock in Maine (Neuman, 1967; van Staal and Fyffe, 1991) and is possibly coincident with ophiolite emplacement (Exploits subzone, Dunnage Zone) onto the Gander Zone margin in Newfoundland (see van Staal and Fyffe, 1991; Colman-Sadd *et al.*, 1992).

Depositional palaeoenvironment

Carbonaceous black shales are commonly interpreted as representing oceanic anoxic events and the Ordovician is particularly bountiful in these rocks (Berry and Wilde, 1978; Berry, 1984; Barnes, 1984; Fyffe and Pickerill, 1993). However, carbon accumulation and preservation can occur in open, oxygenated oceanic environments (Pederson and Calvert, 1990; Lee, 1992). Therefore, other evidence should be used to examine the degree of oxygenation of oceanic waters near or at the site of deposition, for example trace-metal contents (Vine and Tourtelot, 1970; Holland, 1979) or sulphur isotopes (Goodfellow and Jonasson, 1984) to name but two. The significance of ocean anoxia is somewhat controversial but a major transgression with a resultant increase in biologic activity could explain the amount of organic matter and/or stratification of the ocean resulting from geotectonic positioning of the continents near the equatorial regions (i.e., lower oxygen due to increased biologic consumption). This is maintained by the position of the continents that inhibits deep circulation/mixing and oxygenation of the oceanic bottom waters (see Quinby-Hunt *et al.*, 1992).

As previously mentioned, the depositional setting of the massive sulphide deposits may be inferred from the geochemical systematics of some elements within shales. It is well known that carbonaceous sedimentary rocks are usually associated with euxinic or anoxic conditions during sedimentation, especially if the content of organic carbon is high. However, preservation is key to organic accumulation not just biogenic productivity; it is the diversity and relative populations of organisms between anoxic and oxic environments that affect preservation, as well as other seawater processes (cf. Lee, 1992). The S/C ratios in the Patrick Brook and Boucher Brook rocks are similar to other reducing anoxic environments with a possible hydrothermal input (i.e., Black Sea; Hirst, 1974), but dissimilar to those characteristically deposited in oxygenated marine environments (Fig. 13). Reduced carbon (C) is locally high in the Patrick Brook rocks (0.1 to 3.6% C; Fig. 12) similar to other Patrick Brook rocks throughout the Bathurst Camp, whereas the Boucher Brook rocks in this study are generally lower (0.1 to 0.6% C; see also graphitic Boucher Brook slate standard; Fig. 12; Lentz, 1995b) but high enough to impart a medium- to dark-grey to black colouration. This is consistent with the high Fe/Mn contents (>20; Lentz *et al.*, 1995; Fig. 12) that are indicative of low Eh conditions. Therefore, sediments from both formations are deposited in relatively anoxic bottom waters regardless of trace metals they host. In the Patrick Brook rocks, C correlates positively with the base-metals and S (see Table 2), but this is not as apparent in the Boucher Brook rocks possibly because of clastic sulphides in the section. If hydrothermal sulphide deposition is not important, the fixation/formation of sulphides is a function of progessive diagenetic reactions between carbon, organically bound sulphur, and sulphate (?) and ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron (Alpin and MacQuaker, 1993). In turn, these facilitate redistribution of trace metals from their original pre-diagenetic associations (see Chester *et al.*, 1994) and fix a proportion of them into sulphides (Huerta-Diaz and Morse, 1992). The close correlation of some trace metals with S indicates that similar reactions occurred in these rocks.

The increase in CO_2 upwards in the Boucher Brook Formation is possibly related to higher Mg, Ca, and Fe that aids fixation of dissolved carbonate in the sediment at the palaeosurface or during diagenetic/spilitic alteration processes. However, the interpreted occurrence of bedded limestone in the Boucher Brook rocks on Middle River just to the north indicates that carbonates were being deposited at the palaeosurface. The rare occurrence of bedded limestones of the Vallée Lourdes Formation, limestones within the Boucher Brook rocks, and the presence of carbonate in the profile samples suggests that this study section was above the carbonate compensation depth (4 to 5 km or 400 to 500 bars; Bathurst, 1975), unless the basin was also thermally stratified, i.e., higher temperatures promote carbonate saturation. This is a possibility in a stratified basin with continued hydrothermal input at the base (Bischoff, 1969), although it is not likely here because of the general absence of proximal hydrothermal activity and the carbonate increases up-section. However, the general absence of limestones in the section and absence in the lower to upper Caradocian black shale (graptolitic facies) and chert sequence possibly indicates that there was subsidence below the carbonate compensation depth after volcanism.

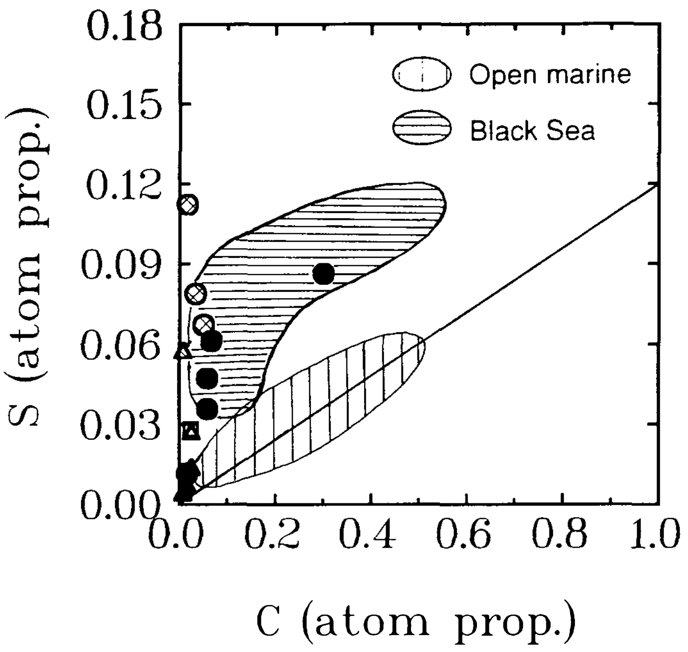

Fig. 13. S (atomic) versus C (atomic) diagram illustrating the distribution of data from the Patrick and Boucher Brook formations. The line (0.12) represents the common S/C ratio for modern marine sediments deposited under oxygenated conditions (Goldhaber and Kaplan, 1974; vertical hatching). Data from Black Sea sediments are from Hirst (1974). See Figure 5 for symbols.

The Boucher Brook sedimentary rocks are high in Mn relative to the Patrick Brook Formation, indicative of hydrogenous Mn precipitation near the transition zone from anoxic to oxic marine conditions. Mn contents are commonly high in the Boucher Brook black shales ($0.13 \pm ^{0.48}_{0.10}$ ppm), particularly from examination of the data in Connell and Hattie (1990) (see Lentz *et al.*, 1995). The sample of Boucher Brook sedimentary rock described by Fyffe (1994) has 1.6% MnO, which is over five times higher than the Patrick Brook samples analysed. It is well known that Mn enrichment in sedimentary rocks is closely associated with the transition zone between anoxic and oxic stratified oceans because of oxidation reactions that drastically affect solubilities (Krauskopf, 1957; Garrels and Christ, 1965; Whitehead, 1973; Quinby-Hunt and Wilde, 1994). In general, the Fe/Mn ratio is a good index of the relative degree of oxidation of various sedimentary rocks, which may be related to seafloor topography in a stratified ocean and degree of convective overturn, as is the present interpretation for Boucher Brook equivalent rocks in the area (Lentz *et al.*, 1995). The anomalous Mn and Fe, as well as other hydrogenous/hydrothermal chemical components within sedimentary rocks of the Boucher Brook Formation is partly a consequence of the amount of mafic volcanism and associated hydrothermal circulation within the volcanic and sedimentary pile. The high proportion of oxidized sedimentary rocks in the Boucher Brook section indicates that wholesale convective overturn of the ocean occurred but quickly re-established anoxic conditions, probably because of increased biogenic activity in warmer metal-rich oceanic water. Alternatively, the mafic volcanism may have been coincident with a buoyant rise of the volcanic centres into oxidized regions of the ocean, which again receded after magmatic upwelling in the back-arc environment. Either of these hypotheses are supported by the transition from red-manganiferous slates and siltstones to black equivalents away from volcanic rocks in the Bathurst Camp (see Force and Cannon, 1988; Spry and Wonder, 1989; Lentz *et al.*, 1995). V, Mo, Ag, and Ni are also locally higher in the Boucher Brook rocks (Lentz *et al.*, 1995) compared to the Patrick Brook rocks, features not observed by Fyffe (1994) or confirmed by this study, although the enrichment of these elements occurs in very specific black shale environments that may not have been sampled in either of these studies.

It is important to note that the red-manganiferous sedimentary rocks of the Boucher Brook Formation are not related to the formation of massive sulphide deposits of the Bathurst Camp, particularly those associated with the Brunswick Belt. Laterally extensive exhalative sedimentary rocks with variable Fe/Mn contents are commonly associated with the massive deposits but are part of the Nepisiguit Falls/Flat Landing Brook stratigraphy (Saif, 1980, 1983; Peter and Goodfellow, 1993, 1996) and may also have spessartine garnet formed locally (cf. Gardiner and Venugopal, 1992).

CONCLUSIONS

The results of this orientation study indicate that there are several geochemical features that may be used for chemostratigraphic and palaeoenvironmental discrimination of slates and siltstones of the Patrick Brook and Boucher Brook formations, as well as describing the paleoenvironment, in particular the palaeo-redox conditions that impact on the formation and preservation of massive sulphide deposits formed in the Bathurst Mining Camp. These are:

(1) The mineralogy of the slates and siltstones, in particular the relative proportions of detrital quartz to phyllosilicates and to a lesser extent feldspar, significantly influences the trace-element systematics in these units.

(2) LREE, HREE, Y, and Th, as well as the LREE/HREE ratios are significantly higher in the Patrick Brook rocks compared to the Boucher Brook rocks, which have chemostratigraphic potential. Using these same elements, the rocks of the Patrick Brook Formation (Miramichi Group) resemble published data on shales associated with the Avalonian basement (i.e., like Gander Zone rocks), whereas the Boucher Brook rocks (Tetagouche Group) more closely resemble shales derived from volcanogenic material (i.e., like Dunnage Zone rocks) with which they are closely associated.

(3) The general absence of feldspar, high Al_2O_3, low Na_2O, coherency of REE's with Al_2O_3 (i.e., not with detrital quartz as inferred from the chemistry), and negative Ce/Ce* for the Patrick Brook rocks supports a tropical source area for these sedimentary rocks. This contrasts with the Boucher Brook sedimentary rocks that contain juvenile felsic to mafic volcanic material, as indicated by the geochemical evidence.

(4) In terms of palaeoenvironment, in this section alone there is an increase in carbonate up-section within the Boucher Brook rocks that possibly has some palaeodepth significance (<400 to 500 bars pressure). Organic carbon is present in both formations but is more abundant in the Patrick Brook rocks. This, together with the sulphur contents that are similar to those of Black Sea anoxic muds, supports deposition within an anoxic environment. However, there is an increase in hydrogenous precipitation of Mn and Ce in the uppermost Boucher Brook rocks indicating they were deposited in a transitional oxic-anoxic environment, where Mn solubility decreases. It seems unlikely that over such a small vertical distance the depositional environment of the Boucher Brook sedimentary rocks would change upward in the stratified ocean. Rather, the extensive felsic and mafic volcanism might increase convective circulation of seawater: (1) within the volcanic pile, thus increasing the metal-rich character of the stratified bottom waters, and/or (2) destabilize the stratification (oxic/anoxic) within the ocean. Alternatively, centres of mafic volcanism may have temporarily buoyantly risen into the oxic zone by thermal upwelling in the back-arc. In either case, this was followed by re-establishment of anoxic conditions within the upper Caradocian Boucher Brook black slates. The higher proportion of hydrogenous components deposited in intermediate anoxic to oxic conditions characteristic of the Boucher Brook sedimentary rocks could help distinguish them from the Patrick Brook sedimentary rocks.

(5) The heavy $\delta^{34}S$ contents of clastic sulphides just above the Flat Landing Brook rhyolite is similar to other massive sulphide deposits in the Bathurst Mining Camp. The intermediate $\delta^{34}S$ of the Patrick Brook rocks could reflect a lower proportion of reduced seawater sulphate (i.e., low SO_4^{2-}/H_2S) in this section compared to Brunswick No. 12 or a higher proportion of biogenic S. The upper Boucher Brook sediments are dominated by negative $\delta^{34}S$ contents, indicative of either a very low proportion of reduced sulphate in the water column or local derivation from sulphate-reducing bacteria.

(6) The highly reducing palaeoenvironment associated with the deposition of Patrick Brook rocks that immediately precede felsic volcanism and formation of massive sulphide deposits, in particular the giant Brunswick deposits, is key to their formation and preservation.

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Armoured mud balls revisited

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Armoured mud balls ranging in size from 2 to 20 cm in diameter (long axis) are common in the upper intertidal zone around Swan Creek, near Parrsboro, on the north shore of the Minas Basin. Shapes vary from nearly spherical to platy to elongate, with elongate predominant. The mud balls form from the action of wave and tidal currents transporting eroded masses of clay, as evidenced by the strike- and dip-parallel orientations of the mud balls with respect to the shore.

Les pelotes de vase blindées d'une taille de 2 à 20 cm de diamètre (axe longitudinal) sont répandues dans la zone intertidale supérieure voisine de Swan Creek, près de Parrsboro, sur la rive nord du bassin Minas. Leur forme varie des pelotes quasi sphériques à celles aplaties et allongées, les pelotes allongées étant néanmoins prédominantes. Les pelotes de vase se forment par l'action des vagues et des courants de marée transportant des masses érodées d'argile, comme en font foi les orientations parallèles aux couches et aux inclinaisons magnétiques des pelotes de vase par rapport au rivage.

[Traduit par la rédaction]

INTRODUCTION

Armoured mud balls, that consist of rounded, pebble-encrusted masses of clay, are unusual clastic sedimentary structures observed primarily in fluvial and tidal settings. Their origin in fluvial environments, in which downstream transport of clay masses produces a nearly spherical shape, has been long recognized (Haas, 1927; Bell, 1940; Pettijohn and Potter, 1964). Additionally, their origin has been documented on shorelines of lacustrine (Haas, 1927; Dickas and Lunking, 1968) and marine environments (Grabau, 1932; Kugler and Saunders, 1959; Hall and Fritz, 1984) where oscillatory motion from wave action produces more elongate shapes. The occurrence of armoured mud balls in the intertidal zone of megatidal coasts has been reported by Thompson (1968) and Stanley (1969). Armoured mud balls in the intertidal zone of the Minas Basin (near Lower Five Islands) have been described by Stanley (1969) who observed the following: (1) a tendency toward bladed and elongate shapes for the mud balls; (2) a tendency for roundness of the mud balls to increase with distance from the high tide mark; and (3) a preferred orientation of the long axes of mud balls parallel to the shoreline. Reports of the occurrence of armoured mud balls in ancient settings are few, although armoured mud balls of Jurassic age have been described in alluvial fan deposits of the Deerfield basin (Little, 1982).

OBSERVATIONS

Armoured mud balls were observed on the north shore of the Minas Basin near the town of Parrsboro on a 50 m long section of beach immediately to the east of Swan Creek, and on a 100 m long section of beach to the west of the creek (Fig. 1). This area is about 11 km west of the area studied by Stanley (1969). The mud balls are found on the upper part of the intertidal zone, in an area where the beach is veneered by pebbly sand, from an elevation just below the high tide mark (in a 10 m tidal range) to the edge of the intertidal mudflat. The armoured nature of the mudballs was easily confirmed by slicing several open. The interior of each mud ball consists of massive clay and the exterior is uniformly coated by a layer of sand to pebble-size clasts up to 25 mm in diameter.

Based on 50 measurements, the mud balls range in size from 2 to 20 cm in diameter (long axis) with a mean diameter of 9 cm. The shapes of these objects are variable and include nearly spherical (compact by the method of Sneed and Folk, 1958), prolate spheroid (platy of Sneed and Folk) (Fig. 2a), and oblate spheroid shapes (elongate of Sneed and Folk) (Fig. 2a, b), the last being the most abundant. The concentration of mud balls averages 0.5 per m^2 across the area in which they occur; however, the distribution of mud balls within this area is irregular.

No clear correlation of distance from the high tide mark with size or shape was observed. Elongate mud balls were observed lying in orientations both parallel to the strike direction of the beach as well as parallel to the dip direction (Fig. 2c). Of 33 elongate mud balls, 15 were dip-oriented, 11 were strike-oriented, and 7 were intermediate. Mud balls with a strike-parallel orientation were observed adjacent to those with a dip-parallel orientation.

Atlantic Geology
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