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PRELIMINARY INSIGHTS INTO LITHOGEOCHEMICAL SIGNATURES AND POSSIBLE PROVENANCE OF REDUCED SEDIMENTARY UNITS ASSOCIATED WITH COPPER MINERALIZATION – WESTERN AVALON ZONE, NEWFOUNDLAND

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ABSTRACT

The Crown Hill Formation of the Musgravetown Group is host to numerous sedimentary-hosted 'stratiform' copper (SSC) mineral occurrences on the Bonavista Peninsula and surrounding areas. The formation is dominated by terrestrial sedimentary successions and localized, stratigraphically extensive lacustrine-type reduced horizons that host most of the copper occurrences, and are termed the Blue Point facies, after the type locality near Duntara.

As a component of a metallogenic study conducted to examine the nature and style of the copper mineralization associated with the Blue Point facies, a series of lithogeochemical samples were collected from the type locality as well as other locations farther south in the vicinity of east Random Island, Little Hearts Ease and Deer Harbour south. For comparative purposes, a suite of samples was also collected from reduced units in the underlying Rocky Harbour Formation. The aim was to document any systematic lithogeochemical signatures associated with the mineralized sedimentary rocks, as well as to investigate the provenance of the different groupings of sedimentary rocks.

Results confirm that specific redox conditions favour precipitation of copper (and possibly Ag and As) as sulphides from mineralized fluids. Samples containing the highest Cu concentrations in this study typically display Fe_2O_3/FeO *ratios in the range of 0.5–0.7, with lower degrees of metal enrichment observed in samples that have lower* Fe_2O_3/FeO *ratios. However, patterns for other metals such as Zn, Pb and Co are not clearly connected to the amounts of ferrous iron.*

Sedimentary rocks of the Blue Point facies contain lower absolute concentrations of SiO_2*,* Na_2O *and* K_2O*, and higher absolute concentrations of* Al_2O_3*,* TiO_2*, MgO, FeO, Ni, Co, Cr, Sc, Nb, Zr, and Eu anomalies (Eu/Eu*), compared to the sedimentary rocks of the Rocky Harbour Formation. This may be indicative of a more mafic source region for the Blue Point facies sedimentary rocks. Similar conclusions may be drawn from tectonic discrimination diagrams using Th* vs. *Sc and La–Th–Sc, as well as on plots using discriminant function analysis. These observations may be important in recognizing equivalents of the prospective Blue Point facies in areas where the stratigraphic context is poorly understood.*

Provenance is only one factor in determining the composition of sedimentary rocks, and this can also be influenced by other syn- and post-depositional processes. More work is required to investigate compositional variations in these rocks and their possible origins.

INTRODUCTION

OVERVIEW

This report summarizes lithogeochemical data collected as part of a study of known sedimentary-hosted 'stratiform' copper (SSC) mineralization and potential mineralized environments in the Avalon Zone, Newfoundland. The study focused primarily on the Blue Point facies of the Crown Hill Formation of the Musgravetown Group, which hosts several occurrences on the Bonavista Peninsula (Hinchey, 2010; Normore, 2010). Stratigraphically equivalent and prospective rocks in the east Random Island, Little Heart's Ease and Deer Harbour south areas were also examined, and reconnaissance work was conducted in the area of the Isthmus of the Avalon Peninsula, and the northeast corner of Fortune Bay near Bay L'Argent (location 6 on Figure 1). Also, marine sedimentary rocks from the Rocky Harbour Formation, below the Crown Hill Formation, were collected for lithogeochemical comparison.

The main goals of the Avalon SSC project were to describe the mineralization at the Blue Point prospect (Hinchey, 2010; Crocker, 2010), and to examine other potentially prospective horizons for similar SSC-style mineralization. Samples were collected for lithogeochemical analysis to determine: 1) if other reduced sedimentary rock units were also anomalous in copper concentrations, 2) if any distinctive lithogeochemical signatures are associated with samples elevated in copper concentrations, and 3) if any inferences could be made regarding the provenance of the various sedimentary rock units.

PREVIOUS WORK

The earliest geological mapping in the area was conducted by Hayes and Rose (1948) who mapped the western portion of the Bonavista Peninsula. This work resulted in stratigraphic correlations between the Bonavista area and the Clode Sound area of Bonavista Bay, which defined the Musgravetown Group. The Geological Survey of Canada (GSC) published a 1:125 000-scale preliminary bedrock map of the entire peninsula (Christie, 1950), and later completed selective follow-up work (*e.g.*, McCartney 1958). All of this work was compiled for 1:250 000-scale maps of the Terra Nova and Bonavista areas by Jenness (1963), who divided the Musgravetown Group into four formations (Cannings Cove, Bull Arm, Rocky Harbour, and Crown Hill formations). The Geological Survey of Newfoundland and Labrador (GSNL) mapped the areas from Bonavista North to Random Island (O'Brien, 1994b, Normore, 2010, 2011, *this volume*), and O'Brien and King (2002, 2004a, b, 2005) placed the late Neoproterozoic rocks into a revised regional stratigraphic framework. King (1988) also produced a compilation map of the Avalon Peninsula, which included the areas around the Isthmus of the Avalon, north to Random Island.

Mineral-exploration programs in the Bonavista area prior to 1999 were of limited extent. A 1989 survey by Cominco Ltd. (Rennie, 1989) followed up lead and zinc lake-sediment geochemical anomalies identified by earlier government surveys. In 1999, Cornerstone Resources Inc. prospectors discovered copper in the redbed successions of the Crown Hill Formation (later termed the Red Cliff Property). The best prospects were drilled under a joint venture with Noranda Inc. in 2001 and 2002, and follow-up work was conducted by Cornerstone Resources Inc. (*e.g.*, Froude, 2001; Dessureault, 2002; Graves, 2003; Seymour *et al.*, 2005). Early drilling results were favourable, and defined a chalcocite-bearing reduced unit containing 0.8% Cu over 9.7 m and 1.0% Cu and 12.1 g/t Ag over 14.25 m; with a higher grade zone containing up to 2% Cu and 23.1 g/t Ag over 6 m. However, mineralization proved difficult to trace laterally. Cornerstone Resources Inc. also targeted other parts of the Crown Hill Formation in the vicinity of east Random Island and around Deer Harbour south (Figure 1), and parts of the underlying Rocky Harbour and Trinny Cove formations, in the vicinity of Port Rexton and Little Hearts Ease. Note that work completed as part of this GSNL study, as well as that of Normore (*this volume*), suggest that some rocks grouped in the Trinny Cove Formation more likely belong to the Crown Hill Formation. In 2010, Cornerstone Resources Inc. optioned the Red Cliff Properties to Vale Exploration Inc. Drilling results from 2010 reproduced low-grade copper mineralization from north of Duntara, but drilling of other prospective reduced horizons did not encounter any significant copper mineralization.

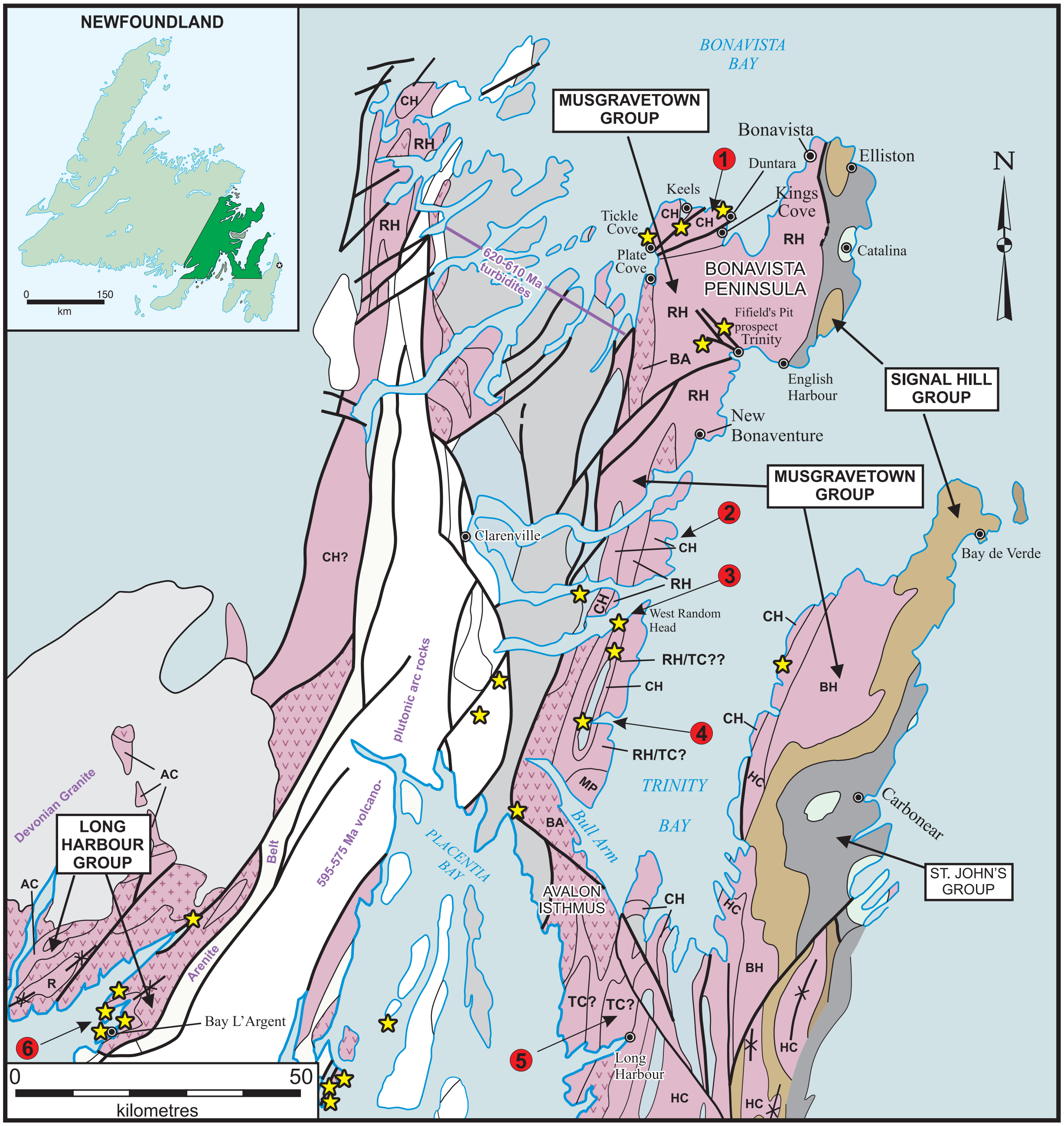
REGIONAL GEOLOGY

The regional geology of the Bonavista Peninsula is summarized from earlier reports by O'Brien and King (2002, 2004a, b, 2005), and Normore (2010, 2011, *this volume*). The Bonavista Peninsula area, from Cape Bonavista, south to Bull Arm, is dominated by late Neoproterozoic (Ediacaran) sedimentary rocks that are in fault contact with older volcanic rocks of the Bull Arm Formation and, with intrusive rocks to the west (Figure 1). The youngest rocks are Cambrian sedimentary rocks preserved within synclinal outliers.

The Neoproterozoic sedimentary rocks fall into two distinct packages. The Conception, St. John's and Signal Hill groups are recognized only on the eastern extremity of the Bonavista Peninsula, from English Harbour, north to Cape Bonavista, and the remainder of the peninsula is underlain by the Musgravetown Group (*e.g.*, O'Brien and King, 2002; Normore, 2010, 2011). These packages are separated by an important regional structure, the Spillars Cove–English Harbour fault zone (*see* Figure 2 in Normore, 2010 and 2011; and references therein). Only rocks of the Musgravetown Group are discussed below.

The Bull Arm Formation is the oldest part of the Musgravetown Group and occurs mostly along the western edge of the Bonavista Peninsula and in the vicinity of the Isthmus of the Avalon Peninsula (Figure 1). It is bounded to the west by the Indian Arm Fault and overlain to the east by the Rocky Harbour Formation (O'Brien and King, 2005). It is dominated by grey-green vesicular basaltic flows (locally columnar jointed) and red-maroon felsic flows and ash-flow tuffs (O'Brien, 1994a).

The north-central portion of the Bonavista Peninsula is dominated by the Rocky Harbour and Big Head formations of the Musgravetown Group. The Rocky Harbour Formation is dominated by grey-green crossbedded marine sandstones and conglomerates that are variably pyritic and, locally, con-



AC = Anderson's Cove Formation
R = Rencontre Formation
CH = Crown Hill Formation
RH = Rocky Harbour Formation
BA = Bull Arm Formation
TC = Trinny Cove Formation
MP = Maturins Pond Formation
HC = Hearts Content Formation
HD = Hearts Desire Formation
BH = Big Head Formation

★ = *copper*

① Blue Point facies - type locality
② Blue Point facies - east Random Island
③ Blue Point facies - Little Heart's Ease
④ Blue Point facies - Deer Harbour south
⑤ Trinny Cove Formation
⑥ Anderson's Cove Formation

Figure 1. *Schematic regional map illustrating the distributions of the main late Neoproterozoic and Paleozoic siliciclastic sedimentary rocks in the northwestern portion of the Avalon Zone (modified from O'Brien and King, 2002). The red dots indicate the general location of the units discussed in the text. For more detailed mapping and map descriptions see King (1988), O'Brien* et al. (*1984*), *O'Brien (1992, 1994b) and Normore (2010, 2011,* this volume*).*

tain disseminated chalcocite mineralization (*e.g.*, Fifield's Pit prospect, Figure 1). Part of this formation was re-interpreted as a thick, coarsening-upward, shallow-marine sequence transitional to the mainly terrestrial rocks of the overlying Crown Hill Formation (*e.g.*, O'Brien and King, 2005); this has been discussed in detail by Normore (2010). The Big Head Formation, found between Bonavista and Trinity is characterized by siliceous and laminated fine-grained marine sandstones.

The Crown Hill Formation outcrops in the area north of Plate Cove and Kings Cove, and in areas south of New Bonaventure through to the Isthmus of the Avalon (Figure 1). The formation is dominated by a coarsening-upward redbed terrestrial succession of mudstone, sandstone and conglomerate (O'Brien and King 2002, 2004a, 2005; Normore 2010). It should be noted that many of the areas included within the Trinny Cove Formation between Random Island and the Isthmus of the Avalon by King (1988), consist of terrestrial redbeds that resemble the Crown Hill Formation; these are reinterpreted as part of the Crown Hill Formation (*see* Normore, *this volume*). The lower Crown Hill Formation consists of thin- to medium-bedded (~0.5–1 m) purple-grey sandstones and red mudstones, which coarsen upward into a red grit, followed by thick amalgamated beds of red-maroon conglomerates. In the area of the Red Cliff properties, north of the town of Duntara, the conglomerates conformably pass upward into red argillite, overlain by two, thick (10 to 15 m) reduced beds of grey-green-brown, laminated argillite and fine-grained sandstone. These grey units are the Blue Point facies (O'Brien and King, 2005; termed the Blue Point horizon within the Red Cliff facies of Normore, 2010) and host disseminated and fracture-hosted copper mineralization (*see* Hinchey, 2010). The facies extends for approximately 9 km across the Duntara Peninsula from north of Duntara to Tickle Cove (*see* location 1 on Figure 1). The reduced units represent a return to anoxic, reducing environmental conditions, and are conformably overlain by coarse-grained, red pebble to cobble conglomerates. The facies also occurs in several areas within the Crown Hill Formation between Random Island and the Isthmus of the Avalon (*see* locations 2, 3, and 4 on Figure 1, *see* Normore, *this volume*).

The Trinny Cove Formation was sampled in the area of Long Harbour (location 5 on Figure 1), where it comprises grey-green to maroon laminated sandstone, locally grading into conglomerate. The stratigraphic relationship between the Trinny Cove Formation in this area and the Crown Hill and Rocky Harbour formations remains unknown. Samples of grey-green sandstone were also collected from the Anderson's Cove Formation of the Long Harbour Group in northeastern Fortune Bay (location 6 on Figure 1) for comparative purposes. The Long Harbour Group potentially represents a stratigraphic equivalent to the Musgravetown Group of the Avalon and Bonavista peninsulas (O'Brien *et al.*, 1994).

CORRELATION OF MAPPED UNITS – CONSIDERATIONS WHEN USING LITHOGEOCHEMISTRY

One of the biggest challenges in attempting to infer information from lithogeochemical analysis of sedimentary rocks stems from the common difficulties of interpreting and grouping sedimentary rocks that belong to the same facies or group, and are derived from a similar provenance. Such correlations of sedimentary facies, which can vary internally over very short distances, are made especially difficult in areas with poor exposure.

In this report, reduced sedimentary rock facies were focused on, and these were divided into two broad groupings: 1) Crown Hill Formation and herein assumed equivalents (*e.g.*, parts of the Trinny Cove Formation of King (1988)) of the Musgravetown Group, and 2) the Rocky Harbour Formation of the Musgravetown Group. Most of the significant SSC mineral occurrences (*e.g.*, Blue Point, Tickle Cove, Little Hearts Ease, Deer Harbour south occurrences; Figure 1) are associated with grey reduced rock facies within larger assemblages of redbeds. Based on facies correlations between the Crown Hill Formation in the northwestern Bonavista Peninsula area, and the redbed assemblages and associated reduced facies in the east Random Island, Little Hearts Ease and Deer Harbour south areas, all significant SSC occurrences (with the exception of the mineralization near Bay L'Argent in Fortune Bay) are interpreted to be hosted by the Blue Point facies of the Crown Hill Formation (*see* Normore, 2010, *this volume*).

Lithogeochemical data presented here is used to draw some interpretations about the provenance, alteration, and redox state of the rock units discussed, however caution is urged due to uncertainties in facies and group correlations.

MINERALIZATION

CHARACTERISTICS OF SEDIMENTARY-HOSTED STRATIFORM COPPER (SSC) MINERALIZATION

Mineralization is largely of the type described as sedimentary-hosted stratiform copper (SSC) deposits. These deposits typically occur as thin (<30 m), peneconcordant sulphide-bearing zones in reduced horizons that are within, or overlie, thick sequences of oxidized continental redbeds. The deposits form as a product of diagenetic to epigenetic deposition of copper (with variable amounts of other metals) from evolving basin- or subbasin-scale fluid-flow systems through the host sedimentary rocks. The reduced host rocks are interpreted as a basin-scale marine or lacustrine transgression into a terrestrial environment, although they may also be 'discordant' reduced zones formed in post-depositional settings (*e.g.*, Brown, 1997).

The source of metals in SSC deposits is largely attributed to the terrestrial redbed sequences that typically occur stratigraphically below the deposits (*e.g.*, Kirkham, 1989; Brown 1993, 1997, 2003; Hitzman *et al.*, 2005). Sulphur may be derived from numerous sources including marine or lacustrine sulphates, or brines formed by the evaporation of these sulphates, pre-existing diagenetic sulphides (pyrite), or hydrogen sulphides in petroleum (Hitzman *et al.*, 2005). Pre-existing diagenetic sulphides are commonly present in the host reduced sediments, where they typically form *via* bacterial sulphate reduction.

Fluids responsible for metal leaching, transport and eventual precipitation are commonly described as oxidized, low-temperature chloride brines. The brines permeate through the redbed sedimentary pile, eventually encountering a reduced horizon that facilitates sulphide precipitation and, dependant upon the metal tenor of the fluids, potential formation of a SSC deposit. Brine circulation may be *via* meteoric recharge, sediment compaction, or local anomalous heat flow; with the first process being preferred by recent deposit models (*e.g.*, Brown, 2003, 2005, 2006).

Mineralization forms through redox reactions and is dominated by copper sulphides (chalcocite, bornite, chalcopyrite and digenite) with lesser amounts of other base-metal sulphides such as galena and sphalerite. Metals are typically zoned relative to the interface of the oxidized footwall redbed rocks and the reduced host rock (*i.e.*, the redoxcline of Brown, 1997). Metals are distributed outward from the interface, from the least soluble to the most soluble sulphides (*e.g.*, chalcocite followed by bornite, followed by chalcopyrite).

SSC MINERALIZATION IN THE AVALON ZONE

Almost all significant SSC-style mineral occurrences known in the Avalon Zone are associated with the Blue Point facies of the Crown Hill Formation. The Crown Hill Formation is dominated by redbed sedimentary rocks interpreted to have formed in continental terrestrial fluvial and/or alluvial fan environments, where the sediments were progressively oxidized to redbeds. The fine-grained grey reduced sedimentary rocks of the Blue Point facies are semi- to concordant with bedding and are interpreted to have formed in a lacustrine-type environment. Such rocks could also form during episodic marine transgressions, but the rapid return to terrestrial redbed facies in the overlying Crown Hill Formation suggests a lacustrine, rather than a submarine environment.

In its type locality, north of the town of Duntara (*see* location 1 on Figure 1), the Blue Point facies consists of two, 10- to 15-m-thick distinct horizons, consisting of very fine-laminated, grey argillite to sandstone. The upper horizon contains a central interval bearing disseminated, fine-grained framboidal pyrite and copper sulphides. The very fine grain size of the reduced sedimentary rocks suggests that they formed in a low-energy environment, with the micro-laminations perhaps being indicative of algal activity. The copper mineralization observed at east Random Island, Little Hearts Ease and Deer Harbour south is similarly associated with localized, fine-grained reduced facies within surrounding redbed sequences. The local stratigraphic context was not previously well defined in these latter areas, and they were placed within the Trinny Cove Formation by King (1988). However, recent mapping by Normore (*this volume*) confirms that they belong to the Crown Hill Formation and are stratigraphic equivalents of the Blue Point facies.

LITHOGEOCHEMISTRY

Lithogeochemical studies investigated the compositions and characteristics of several groups of grey reduced sedimentary rocks, and associated redbed sedimentary rocks, on the Bonavista Peninsula and from other parts of the Avalon Zone. The results discussed in this report represent the following areas (locations highlighted on Figure 1), with the locations of redbed sediments associated with the reduced sedimentary rocks remaining largely undivided.

1) Reduced sedimentary rocks from the type locality of the Blue Point facies of the Crown Hill Formation (location 1 on Figure 1). These are further divided into the upper and the lower reduced beds, as well as the dark-grey mineralized central portion of the upper reduced bed.
2) Reduced sedimentary rocks assigned to the Blue Point facies on the eastern part of Random Island (location 2 on Figure 1), in the vicinity of Little Hearts Ease (location 3 on Figure 1), and in the vicinity of Deer Harbour south (location 4 on Figure 1).
3) Reduced sedimentary rocks assigned to the Trinny Cove Formation by King (1988) (location 5 on Figure 1). As discussed previously, these are equated with rocks included in area 2 above.
4) Reduced grey beds from the Anderson's Cove Formation of the Long Harbour Group; northeastern Fortune Bay (location 6 on Figure 1).
5) Reduced sedimentary rocks (spatially undivided) from the Rocky Harbour Formation of the Musgravetown Group (labelled RH on Figure 1).
6) Reduced grey sedimentary rocks from east of Little

Hearts Ease, in the vicinity of West Random Head (east of location 3, Figure 1). These are interpreted as part of the Rocky Harbour Formation (*see* Normore, *this volume*).

Copper-enriched samples (*e.g.*, >0.1% Cu) from locations 1 and 2 above are representative of regionally distributed reduced horizons within redbed sequences, but the samples with >0.1% Cu from location 5 represent individual hand samples chosen from a reduced facies of probable marine origin. Mineralized samples from location 5 are likely not representative of the Rocky Harbour Formation as a whole. Similarly, copper-enriched samples from location 6 represent individual hand samples collected from showings and are not necessarily representative of the Anderson's Cove Formation.

The first part of this section examines copper (and other metal) concentrations in the various packages of rocks by plotting metals *vs.* Fe_2O_3/FeO (a proxy for the redox state of the rocks), and the second part compares the major- and trace-element compositions (Table 1) of the various groups of sedimentary rocks. Geochemical comparisons are also used as indicators of provenance and are approached in the third part of this section through the use of established diagrams including binary element and ratio plots, ternary molar plots, and discriminant function analysis plots. The discriminant function analysis and the ternary molar plots are based primarily on major elements, whereas the other plots utilize both major and trace elements. Trace elements (*e.g.*, Th, Sc, REE) were used in an attempt to negate secondary sedimentary processes (*e.g.*, diagenesis, *etc.*), and are not directly linked to heavy mineral fractionation processes.

METAL CONCENTRATIONS AND DISTRIBUTIONS

Metal concentrations and distributions within reduced sedimentary rocks from each of the above defined areas were examined by plotting Cu, Ag, Pb, As, Co, V, and Zn against the ratio of ferric (Fe^{3+}) to ferrous (Fe^{2+}) iron. For Ag and Pb, many samples contained concentrations below the detection limits, and these plots do not have as many data points as those for other metals.

In the example of Cu *vs* Fe_2O_3/FeO (Figure 2A), there is a negative correlation observed whereby the Cu concentration increases with ferrous iron (*e.g.*, lower oxidation state, reduced rocks); an observation expected based upon the redox sensitive mechanisms of sulphide precipitation inferred for SSC-type deposits (*see* above). However, the strongest enrichment in Cu concentrations occurs in samples that have a Fe_2O_3/FeO ratio between 0.5–0.7 (Figure 2A). Samples included in this Cu-enriched group come from the dark-grey sulphide-mineralized zone at the Blue Point facies type location, from the Blue Point facies in the Deer Harbour south and Little Hearts Ease areas, and from the Rocky Harbour Formation reduced sedimentary rocks. Not all of the sulphide-mineralized samples from the dark-grey portion of the Blue Point facies are enriched in copper. Samples from the western portion of the type locality of the Blue Point facies (*e.g.*, south of the community of Keels (sample MC-09-022) and from Tickle Cove (09JH-063)) have the highest ferrous iron content, but do not show strong enrichment in copper (Figure 2A). Instead, these two samples fall on the general negative slope trend defined by the other data (Figure 2A).

Silver and arsenic show increased concentrations in the same subset of samples that have increased Cu, again in the Fe_2O_3/FeO range of 0.5–0.7 (Figure 2B, D). In the case of As, the increase is not as significant, and the two samples of the dark-grey sulphide mineralized unit in the western portion of the Blue Point facies display similar levels of enrichment to the samples with Fe_2O_3/FeO between of 0.5–0.7 (Figure 2D). Although not as apparent, lead shows a somewhat similar pattern but the lack of data precludes any definite conclusions.

In the plots of Co, V, and Zn *vs* Fe_2O_3/FeO, there are no systematic linear trends observed and most of the samples have similar concentrations of these elements regardless of oxidation state (Figure 2E–G). The samples from the Rocky Harbour Formation, including those from the area east of Little Hearts Ease, consistently display lower concentrations of all metals (other than Cu) compared to the sedimentary rocks from the other areas (Figure 2A–G).

MAJOR- AND TRACE-ELEMENT COMPOSITIONS

Major- and trace-element compositions of the sedimentary rocks from the studied areas are given in Table 1 and portrayed using box-and-whisker plots in Figure 3. It should be noted that the values presented for quartiles 0 and 4 represent the minimum and maximum values in the dataset, and may represent individual outliers. The data in Table 1 are presented using quartiles and inter-quartile ranges instead of averages and standard deviations, because some elements have log-normal distributions and/or outlying values.

Variations in absolute concentrations of major and trace elements are observed, and these can be used to broadly divide the sedimentary rocks into two main groupings. The first group includes the Blue Point facies of the Crown Hill Formation (observed at the type locality as well as in the Little Hearts Ease, eastern Random Island, and the Deer Harbour south areas) and rocks of the Trinny Cove Formation (Figure 1). The second group includes the Rocky Harbour

Table 1: Major and trace-element compositions (minimum, median, maximum, and inter-quartile range) of the reduced sedimentary units mentioned in the text

	Analytical Method	Upper Grey Beds BPF (N=47, 27)				Dark Grey Mineralized BPF (N=19, 10)				Little Hearts Ease BPF (N=10, 5)				East Random Island BPF (N=6, 3)				Deer Harbour area BPF (N=18, 7)			
		Minimum	Median	Maximum	IQR	Minimum	Median	Maximum	IQR	Minimum	Median	Maximum	IQR	Minimum	Median	Maximum	IQR	Minimum	Median	Maximum	IQR
SiO_2	GS Major (wt. %)	53.72	59.52	69.29	3.27	55.71	57.90	61.70	1.27	57.35	59.52	66.33	2.69	53.56	57.53	61.90	1.48	55.24	60.49	76.79	3.70
Al_2O_3	GS Major (wt. %)	12.94	17.34	19.71	2.06	16.95	17.93	19.66	0.55	14.35	17.79	19.25	1.60	13.63	18.15	19.25	1.37	10.99	17.19	18.57	2.02
Fe_2O_3T	GS Major (wt. %)	5.12	8.48	10.89	1.89	6.93	8.20	9.18	0.56	3.30	7.78	9.46	1.84	4.85	8.74	9.78	2.07	2.80	7.81	9.41	1.15
Fe_2O_3	GS Major (wt. %)	0.32	1.64	9.32	0.90	0.19	2.91	3.20	0.32	0.31	2.10	3.21	1.74	1.39	1.85	3.01	1.24	0.89	2.60	7.55	1.06
FeO	GS Major (wt. %)	0.25	6.27	9.03	1.85	4.43	5.34	8.04	0.39	2.13	5.62	6.24	1.23	2.84	5.74	7.37	1.84	1.21	4.94	6.82	1.80
MgO	GS Major (wt. %)	1.81	3.10	4.26	0.65	2.33	2.74	3.22	0.23	1.56	2.44	3.33	0.21	1.48	2.22	3.69	0.63	0.54	2.33	4.03	0.48
CaO	GS Major (wt. %)	0.11	0.56	1.60	0.46	0.22	0.52	1.79	0.47	0.20	0.99	3.12	0.30	0.82	1.14	5.42	0.32	0.11	1.00	3.16	0.75
Na_2O	GS Major (wt. %)	1.13	2.01	3.24	0.70	1.88	2.15	2.53	0.16	2.15	2.39	3.03	0.24	2.35	2.54	4.46	0.32	1.34	2.29	2.89	0.38
K_2O	GS Major (wt. %)	1.13	2.71	3.71	1.00	2.56	3.11	3.32	0.17	1.73	2.49	3.10	0.59	1.36	2.48	2.76	0.31	0.99	2.41	3.48	0.53
TiO_2	GS Major (wt. %)	0.73	1.37	1.86	0.29	1.00	1.15	1.26	0.06	1.07	1.15	1.44	0.15	0.76	1.19	1.29	0.21	0.34	1.15	1.88	0.11
MnO	GS Major (wt. %)	0.12	0.23	0.38	0.09	0.11	0.16	0.23	0.03	0.09	0.12	0.16	0.02	0.08	0.13	0.28	0.09	0.06	0.11	0.27	0.08
P_2O_5	GS Major (wt. %)	0.02	0.16	0.55	0.14	0.08	0.12	0.60	0.03	0.08	0.11	0.19	0.04	0.02	0.11	0.25	0.04	0.02	0.12	1.26	0.06
Zr	GS Major (wt. %)	159.89	235.09	326.23	36.11	201.97	215.51	355.90	11.85	198.85	215.73	247.49	29.04	175.89	221.23	239.91	20.13	106.30	215.55	286.03	28.55
Ba	GS Major (wt. %)	263.38	648.21	979.53	212.12	572.02	680.11	800.62	76.33	490.33	629.88	801.31	114.82	406.82	635.16	934.70	61.07	224.24	529.81	901.94	167.06
LOI	GS Major (wt. %)	2.53	3.75	4.77	0.44	3.88	4.65	5.34	0.42	2.71	3.76	5.05	1.17	3.17	4.19	5.80	0.86	1.95	3.76	5.10	0.65
Total	GS Major (wt. %)	98.12	98.81	100.61	0.89	98.02	99.12	100.79	0.98	98.07	98.80	99.84	0.94	95.03	98.73	99.06	0.58	98.16	98.63	100.17	0.76
As	GS Trace (ppm)	1.00	4.06	39.45	2.05	14.91	32.00	70.41	16.27	3.59	12.80	46.28	24.30	4.62	22.95	27.29	7.95	2.25	7.57	21.95	8.38
Be	GS Trace (ppm)	0.05	0.87	2.14	1.05	0.43	1.00	1.85	0.93	1.18	1.44	1.75	0.16	1.08	1.53	1.90	0.29	0.95	1.34	1.87	0.32
Co	GS Trace (ppm)	13.79	26.92	55.19	6.30	17.76	26.69	42.69	3.35	22.47	24.72	34.57	3.50	14.02	26.56	43.96	3.79	8.39	24.12	42.01	2.01
Cr	GS Trace (ppm)	34.34	65.90	244.25	26.58	51.85	65.12	75.19	7.96	55.92	77.04	95.24	22.05	32.48	59.87	77.88	16.95	19.73	74.64	124.18	19.00
Cu	GS Trace (ppm)	0.50	48.62	3594.03	113.39	14.88	59.86	14732.15	2566.63	5.63	80.75	5373.35	1021.83	24.03	51.77	97.07	44.65	3.45	79.26	1898.54	171.38
Li	GS Trace (ppm)	35.37	82.66	168.84	23.04	43.93	67.81	77.92	5.98	28.54	40.93	48.07	3.69	32.35	50.21	62.61	10.60	13.28	41.41	58.39	5.61
Nb	GS Trace (ppm)	10.17	15.08	29.39	3.88	11.83	14.26	16.02	1.46	12.37	14.79	15.40	0.43	12.22	14.96	16.91	2.23	5.76	13.89	16.30	2.07
Ni	GS Trace (ppm)	10.18	20.53	27.90	5.14	12.74	22.05	28.51	5.10	12.62	25.10	27.81	5.74	17.93	22.16	29.22	2.32	6.36	21.12	32.54	8.09
Pb	GS Trace (ppm)	0.50	0.50	34.65	0.00	0.50	23.52	69.10	19.11	0.50	0.50	43.29	18.24	0.50	8.51	267.97	9.79	0.50	0.50	20.62	8.93
Rb	GS Trace (ppm)	28.52	74.31	230.22	25.18	65.37	76.92	87.02	7.88	55.95	81.06	98.76	18.09	47.16	80.98	84.51	4.92	24.94	80.04	112.53	19.87
Sc	GS Trace (ppm)	13.53	21.25	27.30	3.14	21.90	24.45	26.27	1.71	17.19	24.52	26.27	1.99	16.62	24.81	26.14	5.47	6.86	21.38	24.23	3.34
Sr	GS Trace (ppm)	58.35	97.04	211.71	31.78	69.45	77.40	164.42	18.81	100.76	162.97	259.26	40.08	167.26	189.40	245.71	27.18	68.31	166.45	247.66	36.32
V	GS Trace (ppm)	96.35	182.65	1246.06	93.84	138.29	156.45	163.71	9.68	143.14	153.37	173.37	3.16	80.86	165.72	180.43	39.16	55.99	144.74	178.15	19.13
Zn	GS Trace (ppm)	72.03	104.84	176.46	24.11	79.09	93.58	185.54	15.57	69.87	78.95	150.73	12.91	50.62	104.31	117.15	29.45	30.66	93.82	166.87	25.82
Ag	GS BPD (ppm)	0.05	0.05	6.45	0.00	0.05	0.16	15.21	4.34	0.05	0.05	2.81	0.30	0.05	0.05	0.38	0.00	0.05	0.05	1.52	0.00
Y	AL 4B2Std (ppm)	25.00	36.00	46.00	8.00	30.00	35.00	39.00	2.00	29.00	32.00	35.00	1.00	33.00	38.00	39.00	3.00	11.00	28.00	32.00	5.50
Cs	AL 4B2Std (ppm)	1.20	2.30	4.80	0.80	1.80	2.15	2.70	0.48	2.20	2.40	3.60	0.60	1.60	2.20	2.40	0.40	1.50	2.50	3.50	0.30
La	AL 4B2Std (ppm)	20.20	30.40	41.50	7.55	18.20	29.00	32.60	6.10	14.20	28.40	33.10	3.20	18.40	27.70	29.30	5.45	5.90	15.90	22.40	8.40
Ce	AL 4B2Std (ppm)	42.50	68.70	88.80	20.65	44.10	64.10	68.10	12.00	31.90	51.30	63.70	13.00	39.80	55.80	67.30	13.75	16.60	32.70	45.60	20.55
Pr	AL 4B2Std (ppm)	5.51	7.79	11.00	2.53	5.31	7.86	8.48	1.59	3.88	6.84	8.01	0.47	5.20	7.39	8.06	1.43	1.63	4.34	5.43	2.40
Nd	AL 4B2Std (ppm)	21.90	31.70	45.20	11.40	21.70	31.15	34.00	6.35	15.70	26.40	30.20	2.60	20.90	29.70	32.30	5.70	6.30	16.30	21.60	8.70
Sm	AL 4B2Std (ppm)	5.20	7.00	9.80	2.60	5.10	6.90	8.00	1.20	4.30	5.80	6.70	0.60	5.40	6.90	7.50	1.05	2.00	4.00	5.10	1.60
Eu	AL 4B2Std (ppm)	1.09	1.67	2.54	0.48	1.24	1.63	2.04	0.32	1.13	1.58	1.66	0.34	1.48	1.83	1.93	0.23	0.47	1.10	1.26	0.32
Gd	AL 4B2Std (ppm)	4.60	6.30	8.90	1.70	4.80	6.45	7.90	0.88	4.50	5.40	6.40	0.70	5.50	6.40	7.10	0.80	2.20	4.30	5.40	1.05
Tb	AL 4B2Std (ppm)	0.70	1.10	1.50	0.20	0.80	1.10	1.30	0.00	0.90	0.90	1.00	0.10	1.00	1.10	1.20	0.10	0.40	0.80	1.00	0.10
Dy	AL 4B2Std (ppm)	4.20	6.20	8.30	1.40	5.20	6.25	7.10	0.48	5.50	5.60	6.10	0.60	5.70	6.50	7.10	0.70	2.00	4.90	5.90	0.85
Ho	AL 4B2Std (ppm)	0.90	1.30	1.60	0.25	1.10	1.25	1.40	0.10	1.10	1.20	1.20	0.10	1.10	1.30	1.40	0.15	0.40	1.00	1.20	0.20
Er	AL 4B2Std (ppm)	2.50	3.80	4.70	0.70	3.30	3.60	3.90	0.38	3.10	3.50	3.70	0.30	3.40	4.00	4.00	0.30	1.20	3.10	3.50	0.65
Tm	AL 4B2Std (ppm)	0.39	0.56	0.71	0.10	0.52	0.55	0.59	0.04	0.48	0.52	0.58	0.06	0.52	0.61	0.62	0.05	0.19	0.48	0.56	0.10
Yb	AL 4B2Std (ppm)	2.70	3.90	5.10	0.55	3.60	3.80	3.90	0.28	3.30	3.50	4.00	0.40	3.60	4.10	4.20	0.30	1.30	3.40	4.00	0.70
Lu	AL 4B2Std (ppm)	0.43	0.63	0.83	0.12	0.58	0.62	0.63	0.02	0.54	0.58	0.65	0.06	0.57	0.69	0.69	0.06	0.22	0.56	0.66	0.09
Hf	AL 4B2Std (ppm)	3.40	6.10	8.20	0.90	5.40	5.75	5.90	0.18	5.10	5.80	6.70	0.90	5.50	5.80	6.00	0.25	2.50	5.70	6.40	0.95
Ta	AL 4B2Std (ppm)	0.60	1.10	1.60	0.25	0.90	0.95	1.00	0.10	0.80	1.00	1.10	0.30	0.80	0.90	1.20	0.20	0.40	0.90	1.30	0.25
Tl	AL 4B2Std (ppm)	0.10	0.30	0.50	0.10	0.30	0.40	0.50	0.08	0.20	0.30	0.50	0.10	0.30	0.30	0.40	0.05	0.20	0.30	0.50	0.15
Th	AL 4B2Std (ppm)	4.40	6.60	15.70	1.20	6.20	6.85	7.50	0.43	6.00	6.50	8.60	0.50	6.60	6.60	6.90	0.15	3.70	6.80	8.50	1.60
U	AL 4B2Std (ppm)	1.20	2.10	4.30	0.50	2.20	2.50	4.20	0.30	2.00	2.20	5.10	0.30	1.90	2.10	2.20	0.15	1.00	2.10	2.50	0.55
Eu/Eu*		0.51	0.77	1.33	0.14	0.63	0.79	0.83	0.05	0.71	0.79	0.85	0.04	0.81	0.83	0.84	0.02	0.61	0.83	1.03	0.09

GS Major and Trace = Analysis via Inductively Couple Plasma-Emission Spectrometry (Methods outlined by Finch (1998))
GS BPD = Basic Partial dilution via HNO_3 with analysis via ICP-OES
Al 4B2Std = Analysis via Inductively Coupled Mass Spectrometry following the dissolution by a lithium metaborate/tetraborate fusion and dilute nitric digestion at Acme Analytical Labs.
GS= Geological Survey Labs , AL= Acme Analytical Labs
N=(number of samples analyzed by GS Major and Trace, number of samples analyzed by AL 4B2Std)
IQR = Interquartile Range (Quartile 3 - Quartile 1)

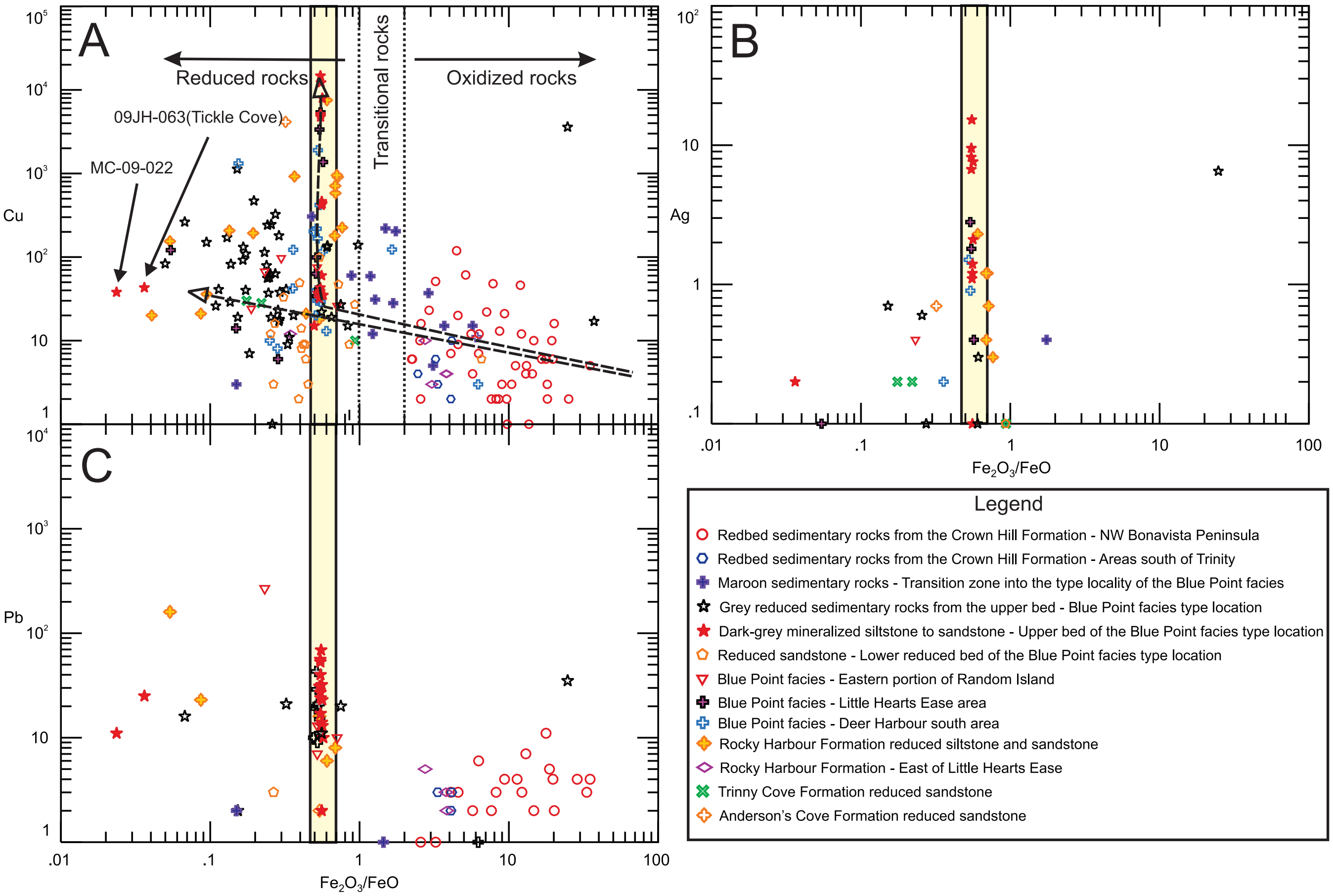


Figure 2. *Geochemical plots of various metals* vs *Fe_2O_3/FeO ratios illustrating the relative affects of redox conditions on metal concentrations in the sedimentary rocks.* See *text for details.*

Formation, and reduced sedimentary rocks from an area east of Little Hearts Ease, which have been assigned to the Rocky Harbour Formation (*see* Normore, *this volume*). The first group of sedimentary rocks (all referred to as various parts of the Blue Point facies) have lower absolute concentrations of SiO_2, Na_2O, and K_2O and higher absolute concentrations of Al_2O_3, TiO_2, MgO, FeO, Ni, Co, Cr, Sc, Nb, and Zr compared to the second group of rocks (*see* Table 1 and Figure 3). For some elements (*e.g.*, SiO_2, Al_2O_3, TiO_2, Ni, Co, Sc, Cr and Nb) the lower reduced bed at the type locality of the Blue Point facies also plots with the second (*sedimentary)* group. For other elements (*e.g.*, Na_2O, Zr), and for europium anomalies (Eu/Eu*), the lower reduced bed of the Blue Point facies shows a more consistent affiliation with the first group.

Samples from both groups have very similar chondrite normalized REE patterns with enriched LREE, negative Eu anomalies, and relatively flat HREE patterns. However, there is variation in the size of the Eu anomaly, which is calculated as Eu/Eu* where $Eu/Eu^* = Eu_{pm}/(Gd_{pm}*Sm_{pm})^{0.5}$, *see* Table 1. The Rocky Harbour Formation has significantly lower Eu/Eu* values compared to the sedimentary rocks from the other areas, including the lower reduced bed at the type locality of the Blue Point facies.

SEDIMENTARY LITHOGEOCHEMISTRY AS AN INDICATOR OF PROVENANCE

Sedimentary lithogeochemistry can be used to infer the provenance of sedimentary rocks and to make comparisons between packages of sedimentary rocks, but it is important to recognize potential external and process-related complications. These may include the transportation of sedimentary grains derived from one or more tectonic settings into a basin that is associated with a different tectonic setting (McLennan *et al.*, 1990), sorting processes that can concentrate heavy minerals, and uncertainties in the behaviour of some elements during sediment diagenesis.

All sedimentary rocks in this study (with the possible exception of those from Fortune Bay) are interpreted to have formed in the same, large sedimentary basin. The Rocky Harbour Formation is interpreted to be older compared to

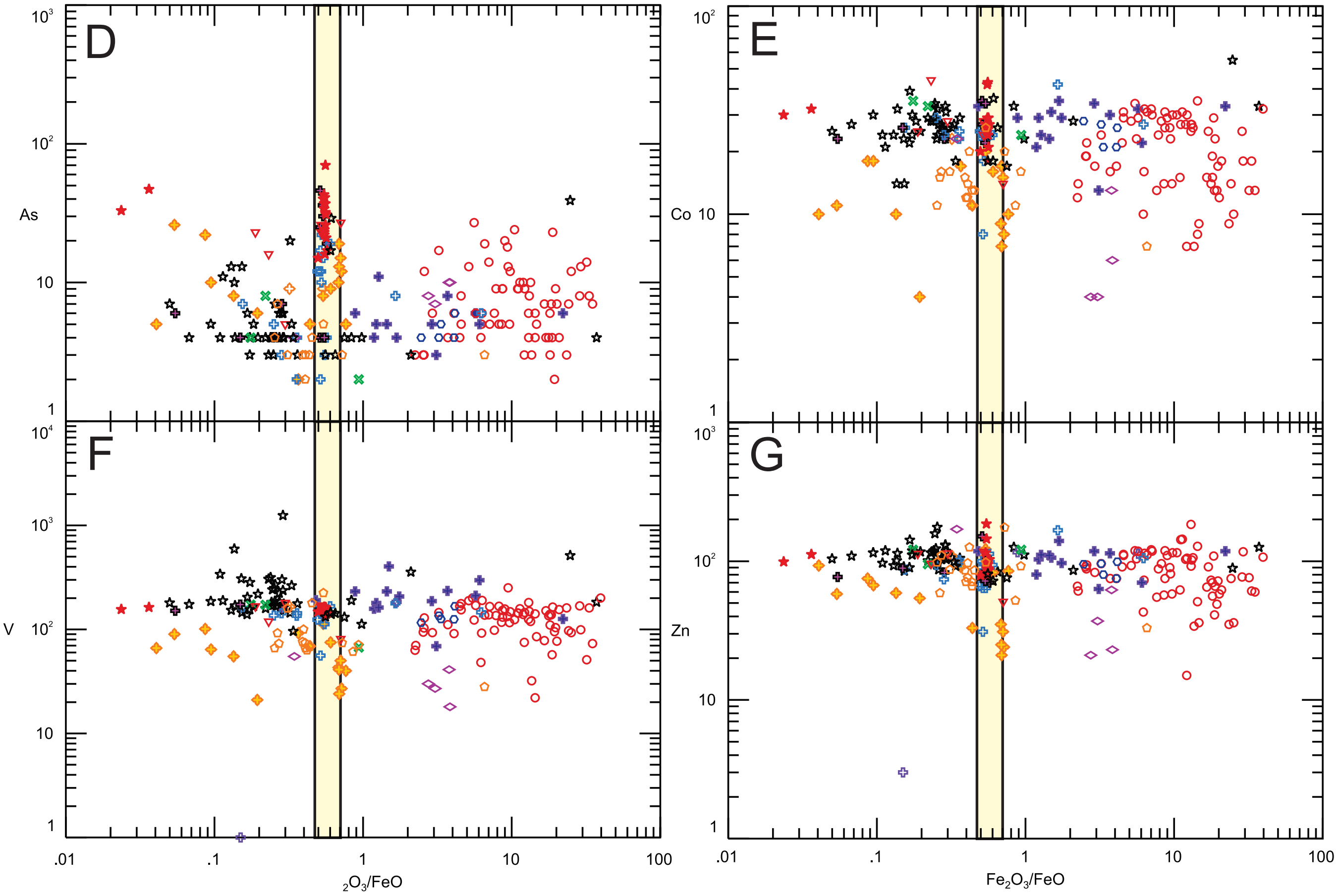


Figure 2. *Continued.*

the Crown Hill Formation; and as such it would have undergone deeper burial and a higher degree of diagenesis. Furthermore, the Rocky Harbour Formation is interpreted to represent a submarine environment whereas the Crown Hill Formation and its equivalents are interpreted to represent terrestrial settings (*e.g.*, Normore 2010, 2011).

It should be noted that for this section of the report only the reduced sedimentary rocks, and in some cases, samples from the Bull Arm volcanic rocks are plotted for comparison.

TiO_2 vs $MgO+Fe_2O_3T$ Plot

In this figure, all samples plot along a linear trend with a positive correlation (Figure 4A). At approximately 8 wt. % MgO + Fe_2O_3T, there is a sharp boundary between the two groupings of sedimentary rocks. The rocks from the Rocky Harbour Formation (including those from east of Little Hearts Ease) and some of the grey beds from the lower portion of the Blue Point facies have <8 wt. % $MgO+Fe_2O_3T$, whereas the rocks from the remainder of the Blue Point facies (upper reduced bed from the type locality as well rocks from the Deer Harbour south, Little Hearts Ease, and east Random Island areas) and those from the Trinny Cove Formation have >8 wt. % $MgO+Fe_2O_3T$.

Cr vs $MgO+Fe_2O_3T$ Plot

This figure displays very similar results as the plot of TiO_2 *vs.* $MgO+Fe_2O_3T$, in that data plots on a positive correlation trend (Figure 4B). As with the previous plot, there is a break in the data at approximately 8 wt. % MgO + Fe_2O_3T.

SiO_2/Al_2O_3 vs SiO_2 Plot

In this figure, all data form a linear trend with a positive correlation (Figure 5). The Rocky Harbour Formation, as well as some of the reduced sedimentary rocks of the lower reduced bed of the Blue Point facies have >65 wt. % SiO_2, with lower values for the remainder of the reduced sedimentary rocks.

Th vs Sc Plot

Figure 6A (adopted from McLennan *et al.*, 1993 and Kasanzu *et al.*, 2008) utilizes variations in the elements Th

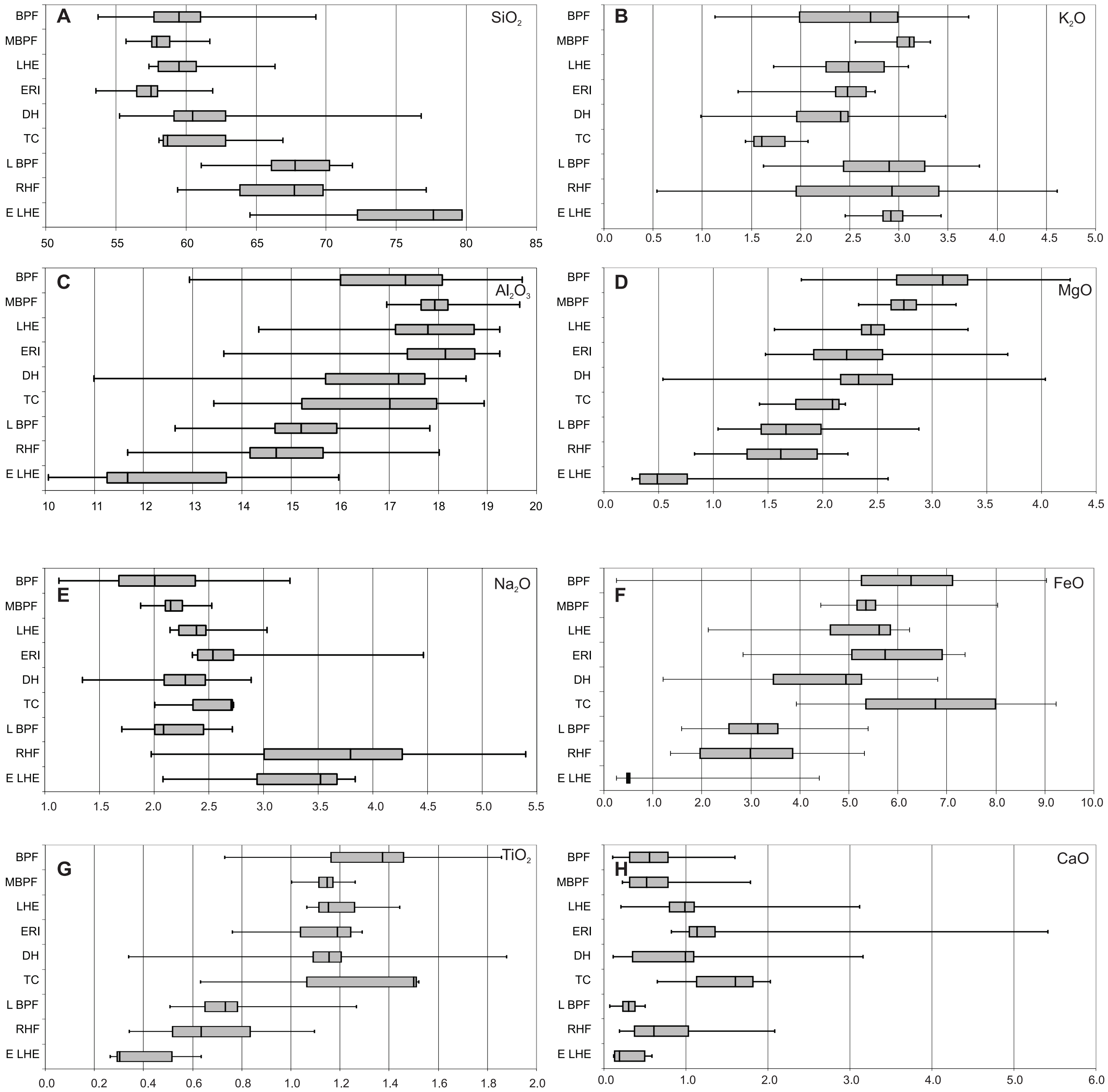


Figure 3. *Box-and-whisker plot comparisons of major-element (weight %, plots A – H) and trace-element (ppm, plots I – O) concentrations for the main sedimentary rock groupings discussed in the text.* See *text for details. BPF=Blue Point facies; MBPF=Mineralized Blue Point facies; LHE=Little Hearts Ease; ERI=east Random Island; DH=Deer Harbour south; TC=Trinny Cove Formation; L BDF=lower grey bed of Blue Point Formation; RHF=Rocky Harbour Formation; E LHE=east of Little Hearts Ease.*

(indicative of a felsic source) and Sc (indicative of a mafic source) as indicators of provenance. Thorium/scandium ratios are known to be indicative of original sedimentary provenance and are not affected by sedimentary processes such as mineral sorting (*e.g.*, *see* Taylor and McLennan, 1985).

On Figure 6A, the Rocky Harbour Formation shows slightly higher Th concentrations and lower concentrations of Sc compared to most of the rocks from the Blue Point facies of the Crown Hill Formation. The lower grey bed from the Blue Point facies also contains significantly less Sc than the remainder of the rocks from that facies. Based on

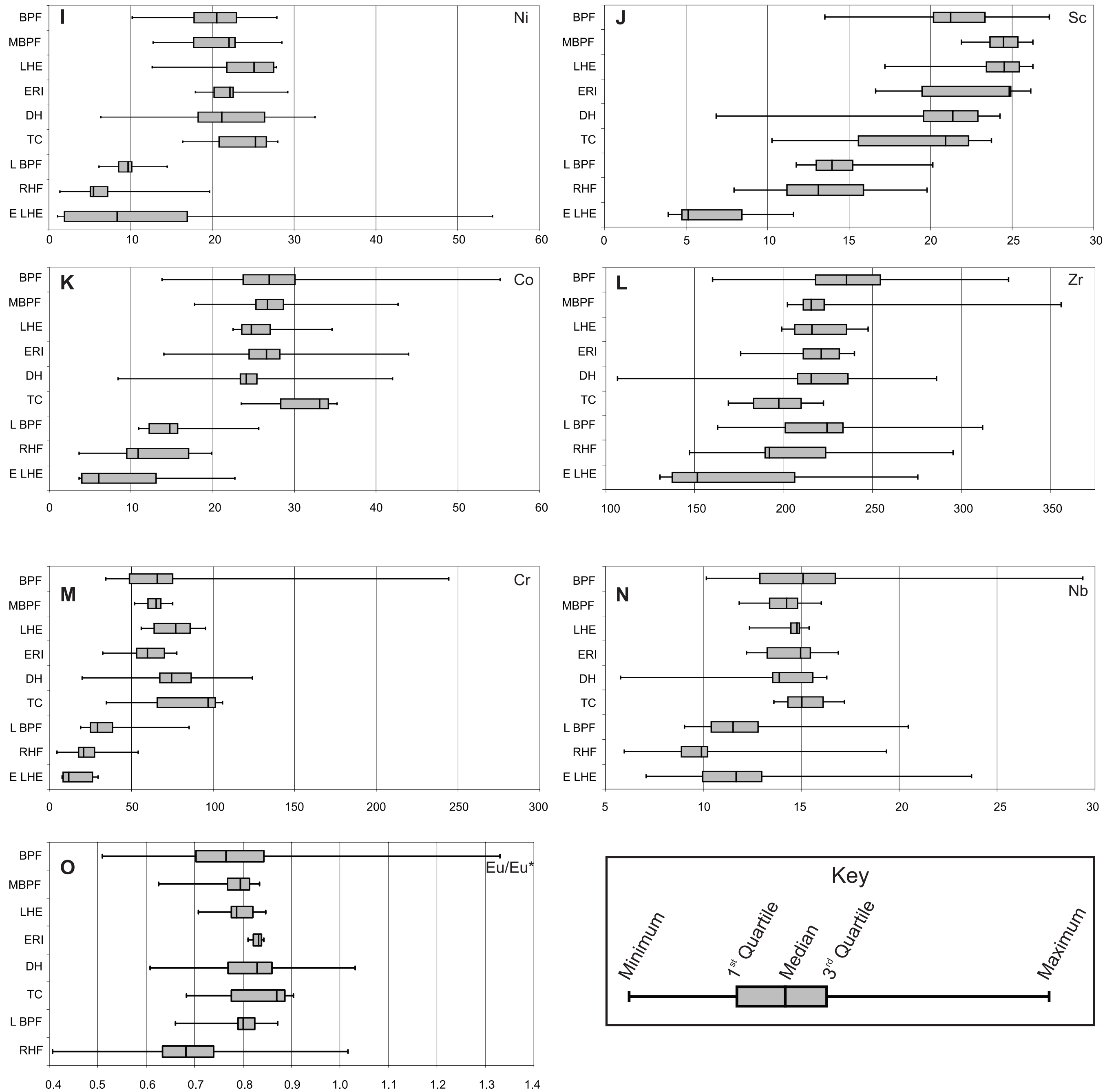


Figure 3. *Continued.*

this plot, the Rocky Harbour Formation is derived from a source (or sources) collectively having an intermediate composition, whereas the Blue Point facies of the Crown Hill Formation is derived from more mafic sources.

La–Th–Sc Plot

Figure 6B (after Taylor and McLennan, 1985, and Bhatia and Crook, 1986) is used to discriminate between felsic and mafic provenances of clastic sedimentary rocks. As with previous plots, samples can be broadly divided into two groups. Samples from the Rocky Harbour Formation predominantly plot in the field for mixed sources (*e.g.*, relatively high La/Sc ratio) whereas samples from the Blue Point facies of the Crown Hill Formation plot have relatively low La/Sc ratios, indicating mafic sources.

Th/Sc vs Zr/Sc Plot

Figure 7 (after McLennan *et al.*, 1993), utilizes the ratios of Th/Sc and Zr/Sc to identify affects of source com-

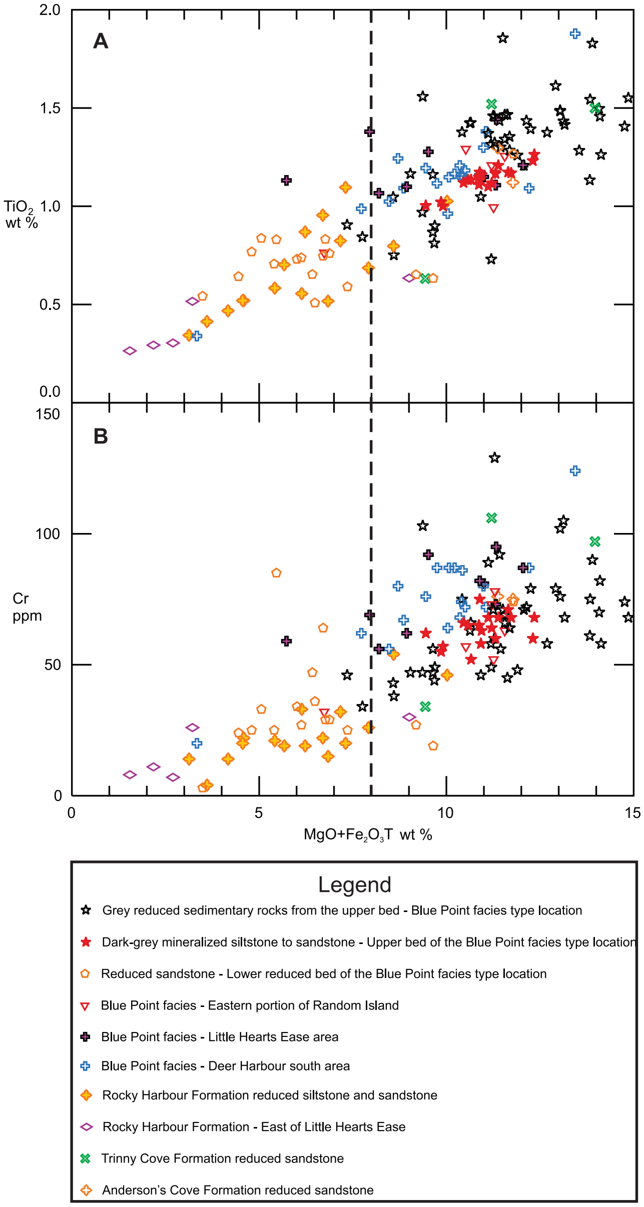


Figure 4. *Plots of* $MgO + Fe_2O_3T$ vs TiO_2 *(A) and Cr (B).* See *text for details.*

position *vs* sedimentary processes on the composition of sedimentary rocks. In typical igneous differentiation processes, both Zr and Th act as incompatible elements compared to Sc, which acts as a compatible element. If sedimentary sorting or recycling occurs, heavy detrital minerals such as zircon or monazite become concentrated in the recycled sediment. As zircon (a mineral enriched in the element zirconium) is present in much higher abundances than monazite (a mineral enriched in thorium) in crustal igneous rocks, sediment recycling would increase Zr relative to Th and would cause the recycled sedimentary rocks to display a trend indicative of zircon addition.

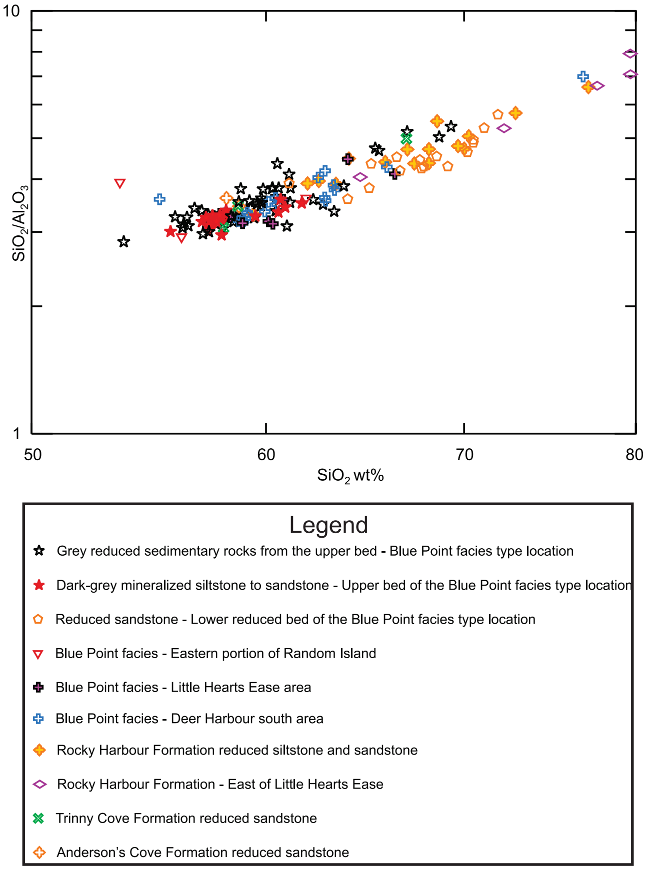


Figure 5. *Plot of* SiO_2 *(wt. %)* vs SiO_2/Al_2O_3. See *text for details.*

In Figure 7, all samples lie along the main trend of compositional variation, indicative of direct contribution from primary source rocks (*e.g.*, no data plot along a separate trend indicative of zircon addition). As with previous plots, the data can be compositionally divided whereby the Rocky Harbour Formation and the lower reduced bed of the Blue Point facies plot with relatively higher Th/Sc and Zr/Sc ratios compared to the remainder of the Blue Point faces. However, the Rocky Harbour Formation actually shows lower absolute concentrations of Zr than the Blue Point facies. The contrast is imparted largely by the lower Sc concentrations in the Rocky Harbour Formation.

Al_2O_3-(CaO^* + Na_2O) – K_2O (or A-CN-K) Ternary Plot

The ternary molar plot A-CN-K is most commonly used to evaluate the influence of chemical weathering on sedimentary rocks (*e.g.*, Nesbitt and Young, 1989; McLennan *et al.*, 2003), but is also useful as an indication of post-depositional metasomatic alteration and modification of major elements during diagenesis (*e.g.*, Fedo *et al.*, 1995). Weathering-dominated trends on this plot typically parallel the A-CN boundary, whereas trends that intersect the A-CN

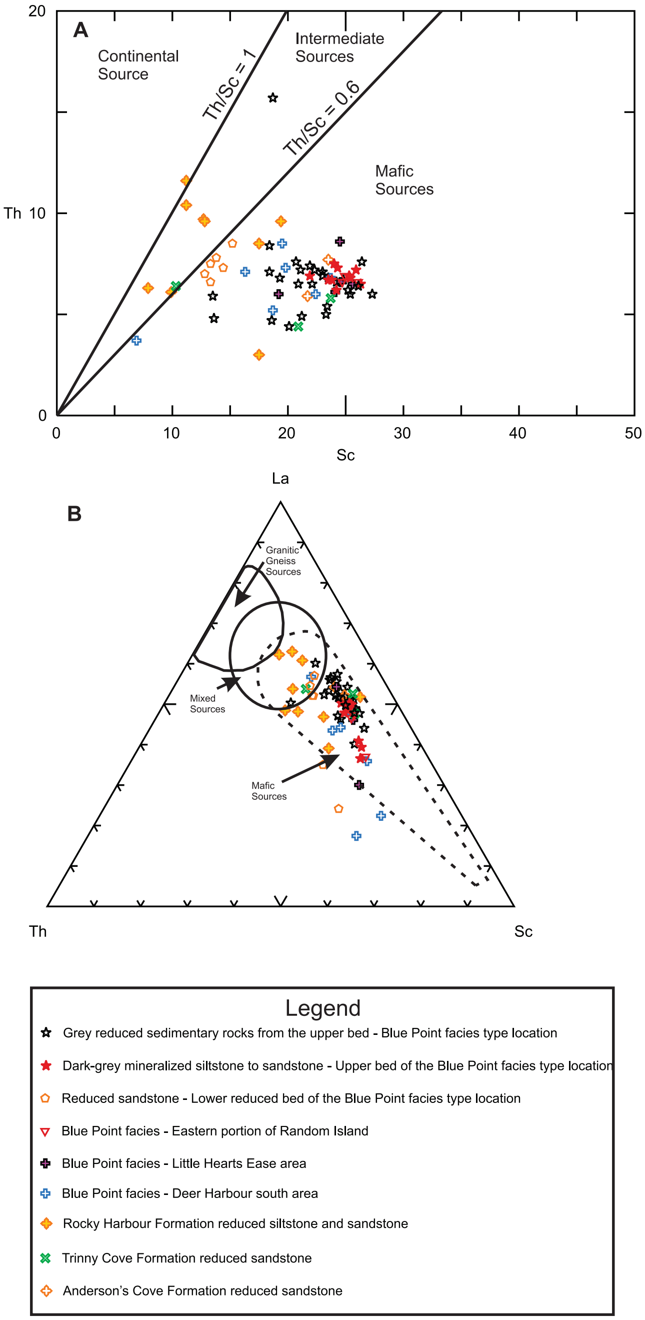


Figure 6. *Paleotectonic discrimination diagrams (all elements in ppm) for the various groupings of reduced sedimentary rocks mentioned in the text. A) Th* vs *Sc plot (adopted from McLennan* et al.*, 1993, and Kasanzu* et al.*, 2008). B) Th-La-Sc ternary plot (after Taylor and McLennan, 1985, and Bhatia and Crook, 1986).* See *text for details.*

boundary are commonly interpreted to be influenced by diagenetic processes or to represent a mixed provenance or grain-size sorting (*e.g.*, McLennan *et al.*, 2003).

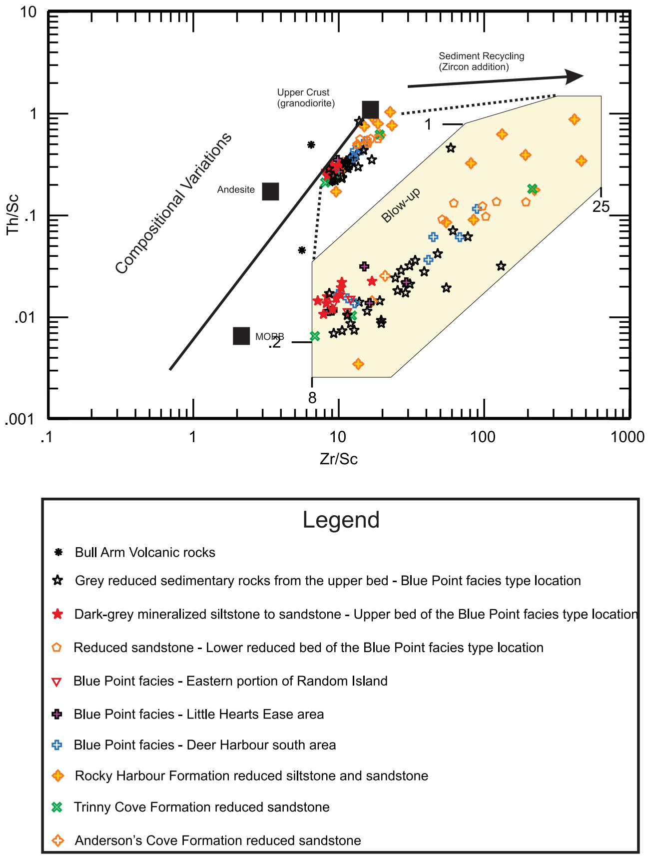


Figure 7. *Th/Sc* vs *Zr/Sc diagram for the various groupings of sedimentary rocks mentioned in the text (after McLennan* et al.*, 1993).* See *text for details.*

Samples of reduced sediments from this study plot on trends that intersect the A-CN boundary, and as such are indicative of processes other than simple weathering (Figure 8A). Although the data are scattered, two main groupings of rocks are identified (Figure 8B, C). Samples from the Blue Point facies of the Crown Hill Formation (including the samples from the lower reduced bed) plot closer to the Al_2O_3 molar apex (also closer to the field for muds from Nesbitt *et al.*, 1996) when compared to samples from the Rocky Harbour Formation, which plot closer to the field for sands as defined by Nesbitt *et al.* (1996). The samples from the Blue Point facies also have a slightly steeper trend line that trends more toward the illite–muscovite mineral fields when compared to the samples from the Rocky Harbour Formation.

Al_2O_3 – (CaO* + Na_2O + K_2O) – (FeOT + MgO) (or A-CNK-FM) Ternary Plot

On this ternary molar figure, commonly used to portray compositional trends involving mafic minerals, samples from the Rocky Harbour Formation plot closer to the feldspar and granite compositions compared to the samples from the Blue Point facies (Figure 9). The reduced sedimentary rocks from the lower grey bed of the Blue Point facies plot close to the remainder of the Blue Point facies, rather than with some of the samples from the Rocky Harbour Formation, as seen in Figures 3–7. This data provide the best discrimination between the two groups of sedimentary rocks.

Discrimination Diagrams

The two discrimination diagrams of Roser and Korsch (1988) use discriminant function analysis of major-element data to assign provenance signatures to clastic sedimentary rocks. In a review of the reliability of discrimination diagrams for determining tectonic depositional environments of sedimentary rocks (Ryan and Williams, 2007), plots using major elements were found to more accurately reflect the tectonic setting of samples than many plots using trace elements. For details of the method and for definition of the functions plotted in Figure 10, *see* Roser and Korsch (1988).

The first plot (Figure 10A) uses major-element oxides for the discriminant function analysis and results in a scatter of data in all four of the defined fields. In detail, however, there is a separation of the data with samples from the Rocky Harbour Formation predominantly plotting within the field of felsic igneous provenance and the samples of the Blue Point facies clustering around the triple junction of the other three fields. The second plot (Figure 10B) uses functions of oxide/Al_2O_3 ratios, and it also results in a scattering of the data. In this plot, the data is again separated with the Rocky Harbour Formation predominantly plotting in the field of felsic igneous provenance whereas the samples from the Blue Point facies plot between the fields for intermediate and mafic igneous provenance. In both plots the sedimentary rocks from the lower reduced bed of the Blue Point facies plot between the Rocky Harbour Formation and the remainder of the Blue Point facies samples. The boundaries with the field for quartzose sedimentary provenance in these figures are generally viewed as being gradational in order to compensate for highly siliceous volcanic sources.

DISCUSSION

CONTROLS ON MINERALIZATION

Based on the plots of metals *vs* Fe_2O_3/FeO (Figure 2), it is apparent that Cu concentrations are correlated with increased ferrous iron, suggesting that specific redox conditions are required for the precipitation of Cu sulphides. Similar patterns are indicated for Ag and possibly As, but are not obvious for other metals. A narrow range of Fe_2O_3/FeO seems to be associated with the strongest Cu and Ag enrichment. Not all sulphide (pyrite) mineralized samples of the Blue Point facies plot in this range, and those that do not are not strongly enriched in Cu concentrations, as illustrated by some of the sulphide (pyrite) mineralized samples from the central portion of the upper reduced bed of the Blue Point facies in the type locality (*e.g.*, samples MC-09-022 and 09JH-063 on Figure 2A). Additional controls on copper-rich sulphide precipitation may include host-rock porosity and permeability, structural ground preparation prior to mineralized fluid introduction, and other compositional variations amongst reduced sedimentary rocks in a certain locality. Field evidence from this study suggests that as reduction fronts transform ferrous (Fe^{3+}) iron to ferric (Fe^{2+}) iron (a transformation observed *via* the reduction of magnetite crystals to pyrite (*see* Plate 13A and B *in* Hinchey, 2010), redox conditions favour copper precipitation.

Finally, there are indications from geochemical data that the Crown Hill Formation generally displays higher metal concentrations than the underlying Rocky Harbour Formation. This may be significant in the context of models that suggest derivation of metals in SSC deposits from the adjoining redbed sequences.

IMPLICATIONS FOR PROVENANCE

Based on the absolute concentrations of major and trace elements (Table 1, Figures 3–6), it is apparent that the Rocky Harbour Formation contains lower concentrations of TiO_2, Al_2O_3, FeO, Zr, Sc, Ni, Co, Cr, and europium anomalies (Eu/Eu*) when compared to the Blue Point facies of the Crown Hill Formation. Since these major oxides and trace elements are known to be normally enriched in mafic rocks compared to felsic rocks (*e.g.*, *see* Rollinson, 1993), it could be inferred that the source region for the Blue Point facies had a more mafic bulk composition, compared to a more felsic composition in the source regions for the Rocky Harbour Formation.

The higher SiO_2 concentrations and generally lower trace-element concentrations in the Rocky Harbour Formation compared to the Blue Point facies could also be indicative of an increased proportion of quartz and feldspar and a decreased proportion of clay minerals in the Rocky Harbour Formation. This would suggest a higher degree of textural maturity compared to the Blue Point facies. Limited petrographic examination suggests that the Blue Point facies samples contain a higher portion of very fine-grained clay minerals and increased epidote, whereas the matrix of the Rocky Harbour Formation samples is more siliceous. This observation is indirectly supported by the positioning of samples on the A-CN-K and A-CNK-FM plots (Figures 8 and 9). However, if textural maturity and sediment reworking did influence the chemical compositions of the groups of sedimentary rocks, it is not evident on the plot of Th/Sc *vs.*

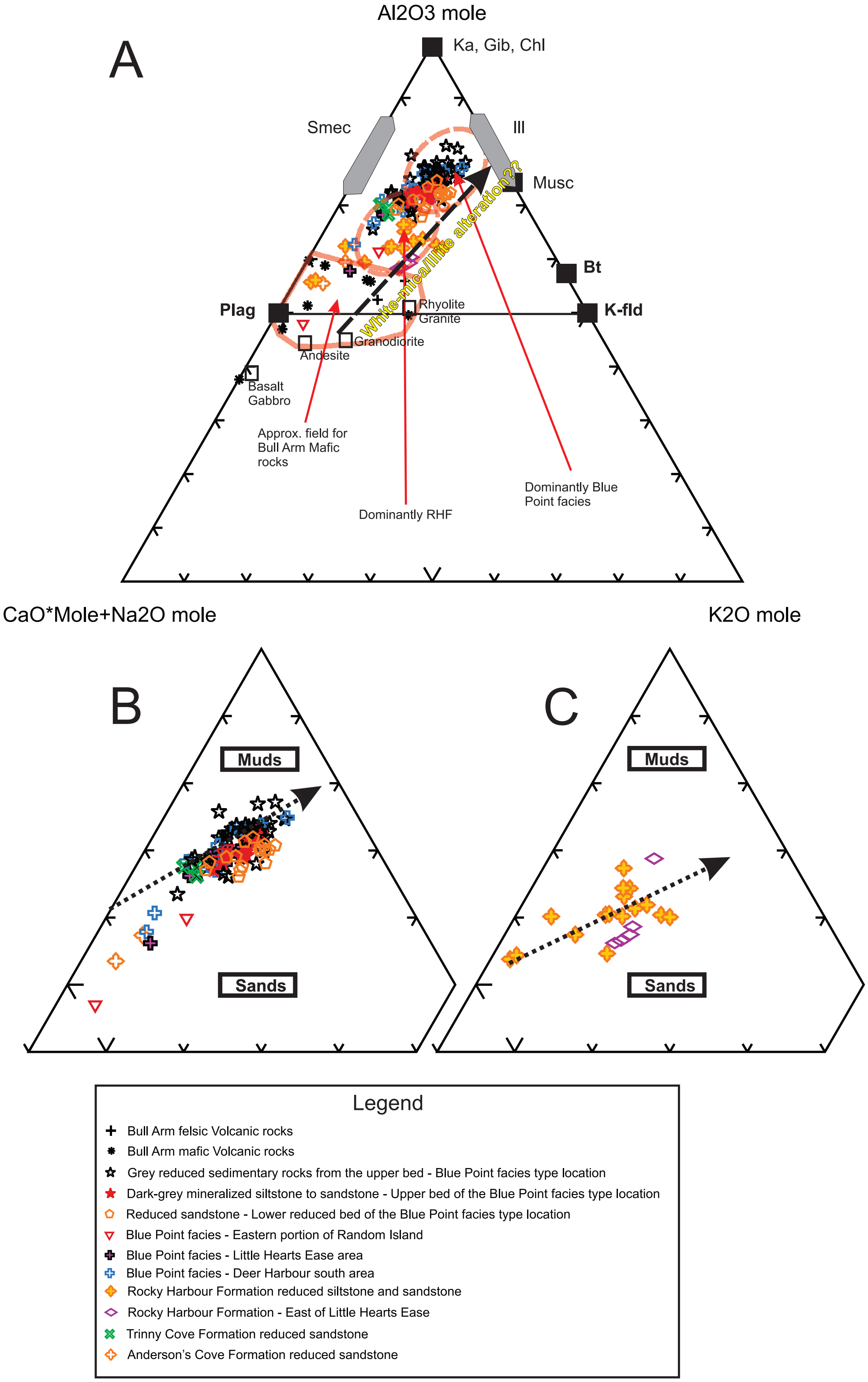


Figure 8. *A) A-CN-K ternary molar diagram (after Nesbitt and Young, 1989; Nesbitt* et al., *1996; McLennan* et al., *2003) plotting the compositions of the various groupings of reduced sedimentary rocks discussed in the text. Note that in the blow-up Figure 8B and C that two groupings of sedimentary rocks can be defined.* See *text for details. Mineral compositions are indicated by boxes and shaded shapes and include: Ka = kaolinite; Gib = gibbsite; Chl = chlorite; Ill = illite; Musc = muscovite; Bt = biotite; K-fld = potassium feldspar; Plag = plagioclase; Smec = smectite.*

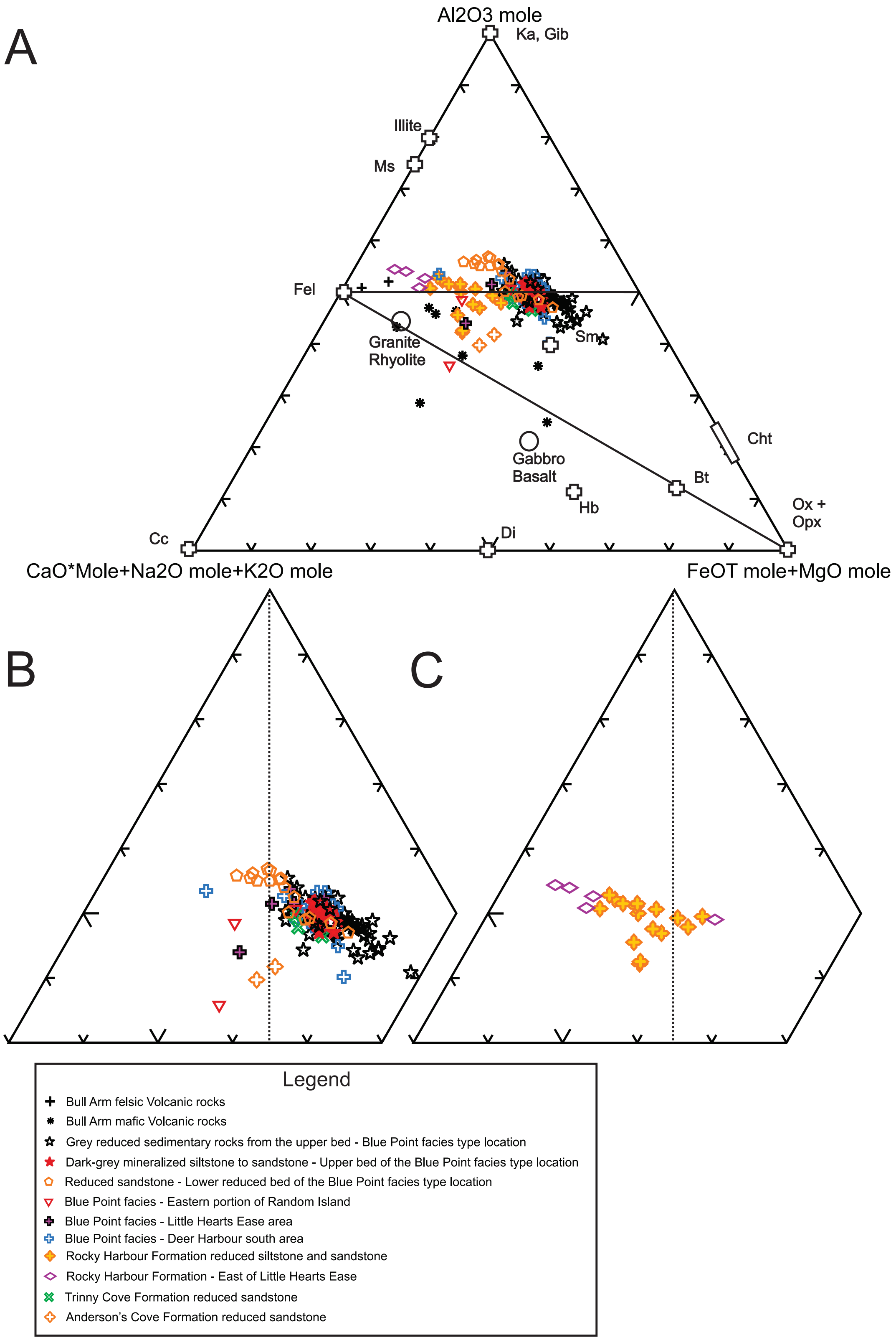


Figure 9. *A) A-CNK-FM ternary molar plot (after Nesbitt, 2003 and references therein). Note that in the blow-up Figure 9B and C that two groupings of sedimentary rocks can be defined.* See *text for details. Mineral compositions are indicated by boxes and shapes and include: Ka = kaolinite; Gib = gibbsite; Chl = chlorite; Ox = Fe-oxides; Opx = orthopyroxenes; Bi = biotite; Hb = hornblende; Di = diopside; Cc = calcite; Fel = feldspars; Ms = muscovite; Sm = smectite.*

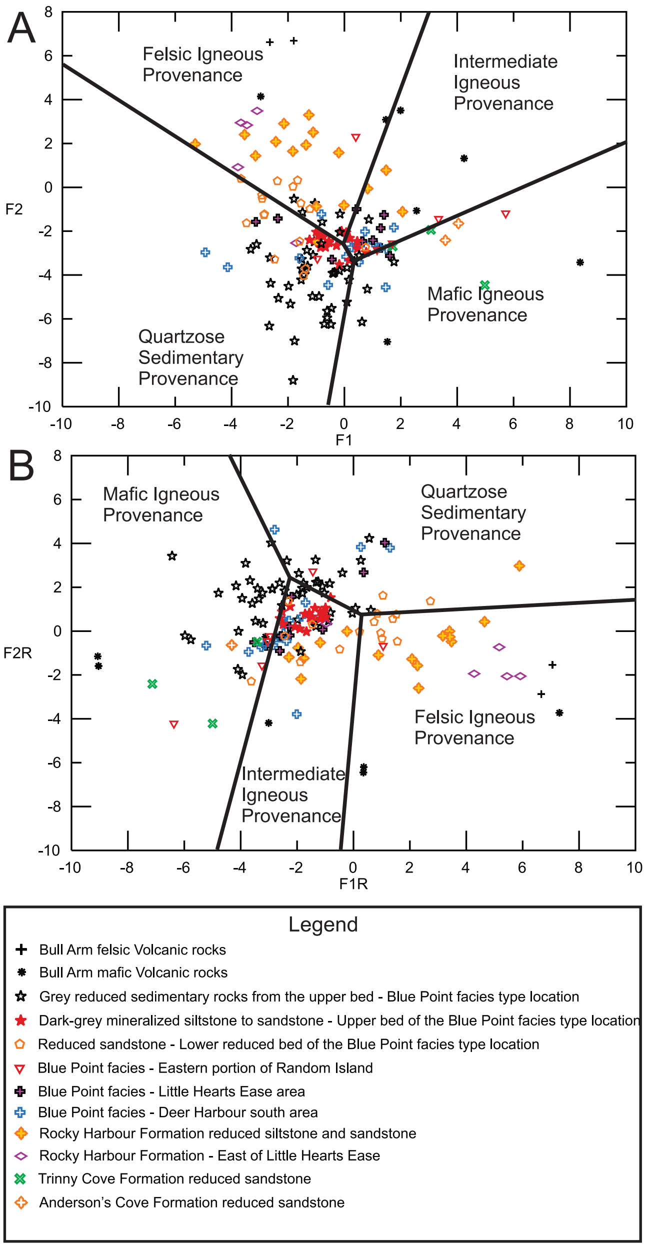


Figure 10. *A) Discriminant function analysis diagram (after Roser and Korsch, 1988) using major-element oxides from all the groupings of reduced sedimentary rocks in the text. B) Discriminant function analysis diagram (after Roser and Korsch, 1988) using functions of oxide/*Al_2O_3 *ratios of all the reduced sedimentary rock groupings discussed in the text.* See *text for details. For definitions of the functions plotted see Roser and Korsch (1988).*

Zr/Sc (Figure 7) as there is no increase in zirconium concentration observed for the Rocky Harbour Formation samples (*see* also Table 1). The preferred interpretation for the geochemical contrasts outlined in Figures 3 to 9 is that these two main groupings of sedimentary rocks differ in their provenance.

The Rocky Harbour Formation has a significantly lower europium anomaly (Eu/Eu*) signature compared to all of the rest of the sedimentary rocks, including the lower bed at the type locality of the Blue Point facies (Table 1, Figure 2). It is known that the most important factor contributing to the REE concentrations of clastic sedimentary rocks is their provenance (*e.g.*, *see* McLennan *et al.*, 1993; Asiedu *et al.*, 2000). The Eu anomaly in sedimentary rocks is assumed to be inherited from the source regions. The larger negative Eu anomaly in the Rocky Harbour Formation sedimentary rocks is suggestive of a more differentiated (*i.e.*, felsic) source region because these would contain igneous rocks that typically show this type of pattern.

Although the data presented largely support the lithogeochemical groupings discussed above, the lithogeochemical signature of the lower reduced bed at the type locality of the Blue Point facies is somewhat problematic. Whereas the sedimentary rocks of this lower reduced bed are compositionally similar to the remainder of the Blue Point facies for some elements (*e.g.*, Na_2O, Eu/Eu*), they commonly have compositions that fall in between those of the remainder of the Blue Point facies and the Rocky Harbour Formation, and in many cases are closer to the latter. As such, as with all lithogeochemical studies, especially those involving sedimentary rocks of unknown sources and affinities, it is acknowledged that many factors, both internal and external as well as syn- and post-depositional, can influence geochemical signatures associated with various packages of rocks, and results such as those presented here must be interpreted with caution.

CONCLUSIONS

Results from this study suggest that sedimentary lithogeochemical studies may provide insight into the provenance histories of sedimentary units found in the Avalon Zone. Specifically, geochemical discrimination diagrams suggest that reduced units in the Rocky Harbour Formation may have been sourced from a relatively more felsic-source terrane compared to the source terrane for the Blue Point facies of the Crown Hill Formation. This feature may prove useful in determining the stratigraphic affinity of such sequences in areas where external relationships are not well understood. It may also have importance in assessing the mineral potential of such rocks elsewhere in the Avalon Zone as almost all significant SSC mineralization discovered to date is associated with the Blue Point facies, rather than the Rocky Harbour Formation.

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