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TRACE- AND RARE-EARTH-ELEMENT GEOCHEMISTRY OF THE LAWRENCE HARBOUR FORMATION, EXPLOITS SUBZONE: PRELIMINARY REPORT

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ABSTRACT

Preliminary data from the trace- and rare-earth-element (REE) geochemical analyses of black shale samples from the Lawrence Harbour Formation of central Newfoundland have been obtained. Data collected were plotted as a series of extended REE diagrams and in ternary discriminant plots to determine the depositional setting, and to examine the possibility of geochemical fingerprinting of the unit. Fifteen shale samples have been analyzed, including samples from the Late Ordovician Lawrence Harbour Formation, age-equivalent units in Scotland, and black shale (forming the matrix) of the Dunnage Melange. The preliminary results illustrate essentially similar geochemical compositions for most of the Late Ordovician shales from Newfoundland and Scotland and from the matrix of the Dunnage Melange, which suggest a mature (calc-alkaline) island-arc setting for these rocks.

INTRODUCTION

The Late Ordovician black shale unit (Caradoc shales) of the Exploits Subzone (Dunnage Zone) of central Newfoundland has been widely used as a marker horizon during regional mapping studies, and has been the subject of a number of previous studies relating to its potential as a host to sulphide mineralization (e.g., Dean and Meyers, 1982). It has also been the focus of graptolite studies for over a hundred years (Murray and Howley, 1881; Erdtmann, 1976) and has been used to define a series of Late Ordovician graptolite biozones for the region (S.H. Williams, 1995). S.H. Williams (1995) considered that most black shales of this age in the Exploits Subzone could be included within a single formation, and suggested expanding the use of the stratigraphic name Lawrence Harbour Formation. However, almost all the exposures of the unit are heavily deformed, and in many cases the shales are cleaved too strongly for preservation of identifiable, biostratigraphic diagnostic graptolites. This is particularly true for many of the exposures of black shale on, and around, New World Island, the forested tracts southeast of Millertown, and in the Baie d'Espoir region. In the latter region, Williams (1991a) recovered probable Late Ordovician graptolites from a number of localities.

In order to demonstrate that other Late Ordovician shale units in central Newfoundland are correlatives of the Lawrence Harbour Formation, additional data are required, either in the form of detailed petrological studies or by geochemical fingerprinting of the unit, using parameters that would be essentially unaffected by low-grade regional metamorphism.

METHODS

Sediment composition is influenced by several first order processes, including weathering, source-rock composition, sorting, and diagenesis (Johnsson, 1993). These are influenced by the tectonic setting of source regions, transportation systems and depositional environment, but all operate as an intergrated system (Johnsson, 1993). Even though these processes operate together in varying the geochemical characteristics of sediment, correlations between sediment composition and tectonic setting are often observed (e.g., McLennan *et al.*, 1990; André *et al.*, 1986). The use of rare-earth-element (REE) data in determining provenance and tectonic setting has been well documented in recent geochemical studies of sediments. Much of this work has involved the use of sand and mud fractions of deep-sea turbidites (e.g., Williams *et al.*, 1996; McLennan *et al.*, 1990). In the past, fine-grained sedimentary rocks have rarely been used in petrographic studies. The more traditional application of shales commonly involves use of the unit as a correlative horizon, and where fossiliferous, as a biostratigraphic marker horizon (e.g., Williams, 1991b). With the increasing focus on sediment geochemical studies, the use of shales in determining provenance and tectonic setting has become more appeal-

ing. André *et al.* (1986) and McLennan *et al.* (1993) have shown that shales are reliable indicators of provenance and tectonic setting, provided there is a component of fine-grained terrigenous sediment present (i.e., the sediment is not entirely pelagic in origin).

In this paper, preliminary results are presented from trace and REE analysis of black shales from the Lawrence Harbour Formation, several age-equivalent samples from Scotland, and a number of Silurian and earlier Ordovician shales.

TECTONIC SETTING

The geology of central Newfoundland is represented by units that comprise the early Paleozoic Dunnage Zone, subdivided into the Exploits and Notre Dame subzones. The units within both subzones are structurally modified and have been interpreted as a composite of oceanic terranes representing the vestiges of the Iapetus Ocean (H. Williams, 1995). The Late Ordovician history of the Exploits Subzone is recorded as a sequence of conformable chert overlain by black shales that are in turn overlain by a sequence of turbidites. The geology of the Lawrence Harbour Formation of the Exploits Subzone has been studied by Kean and Jaysinghe (1982), and most recently by Dixon (1994), Williams and O'Brien (1994) and S.H. Williams (1995). It consists of folded and thrust-faulted black and silty shales that span four graptolite biozones (S.H. Williams, 1995). These shales are underlain by Middle Ordovician rocks of the Victoria Lake Group (Kean, 1977) and the Lawrence Head Volcanics (O'Brien *et al., in press*), with the transition marked by a distinct unit of grey bioturbated chert. The Lawrence Harbour Formation is everywhere overlain by Upper Ordovician turbidites of the Point Leamington Formation, the transition being marked by the first occurrence of distinct, thick sandstone beds directly overlying black shales of the Lawrence Harbour Formation (Williams, 1991b). A similar tripartite stratigraphic sequence also exists over similar time intervals in the British Isles (Colman-Sadd *et al.*, 1992). Ongoing structural investigation of the Lawrence Harbour Formation and associated units in the central Exploits Subzone by one of us (JEC) indicates a predominant axial-planar cleavage associated with regional, northeast-verging folds. This cleavage maintains its orientation across thrust faults providing some indication of relative timing to deformation events affecting these units.

In addition to the Lawrence Harbour Formation, there are several other broadly age-equivalent black shale sequences throughout the Exploits Subzone including the Shoal Arm and Dark Hole formations, the Rodgers Cove Shale and several unnamed units. Although these exhibit the same biostratigraphic divisions, it is difficult to determine correlative units due to the structural complexity and sparse outcrop exposure throughout the area. In southern Scotland, the Moffat Shale Group appears to be a correlative of the Lawrence Harbour Formation, at least in terms of its Caradoc stratigraphy, (Colman-Sadd *et al.*, 1992; S.H. Williams, 1995). The Newfoundland unit is essentially equivalent to the Glenkiln and Lower Hartfell formations. In the Southern Uplands, many of the more southerly tracts reveal extended shale deposition reaching into the Early Silurian (Llandovery) before the onset of greywacke deposition; a number of northern regions are, however, similar to central Newfoundland with shale deposition restricted to the Caradoc (Leggett *et al.*, 1979; Armstrong *et al.*, 1996). The Moffat Group was originally considered to have been deposited in a deep open-ocean environment, but recent studies have suggested a more likely relation to an accretionary prism (McKerrow *et al.*, 1977) or intra-arc setting (McKerrow, 1987; Armstrong *et al.*, 1996; Williams *et al.*, 1996).

The Dunnage Melange is defined as a major slump composed of clastic and mafic volcanic rocks within a shale matrix (H. Williams, 1995), which is overlain by Upper Ordovician shales in the northwest Exploits Subzone (Horne, 1969). There have been several ages provided for blocks within the melange (e.g., Kay and Eldredge, 1968; Hibbard *et al.*, 1977; H. Williams, 1995) but the source of the matrix shales is unclear. Recent isotopic dating of the Coaker Porphyry (an intrusion contemporaneous with melange emplacement) suggests an Early to Middle Ordovician time of formation (H. Williams, 1995). A single sample of Dunnage Melange matrix shale has been analyzed for trace-REE in this study.

PRELIMINARY RESULTS

The only previous sediment geochemical study done in the region consisted of major- and trace-element analysis of samples from the pre-black shale argillites and chert in order to define the tectonic evolution of the Shoal Arm Formation (Bruchert *et al.*, 1994). For the present investigation, 15 samples (collected by JEC and SHW) were assembled for XRF and ICP-MS analyses of trace- and rare-earth elements; Scottish specimens were collected by SHW. All samples were taken from localized outcrops with the intention of obtaining a small representative population of Lawrence Harbour and equivalent shales for preliminary geochemical analysis. Earlier Ordovician and Early Silurian samples were included as controls to test homogeneity in the composition of shales belonging to other stratigraphic units (Figure 1b). All data were normalized to primitive mantle values (Sun and McDunough, 1988) as this best reflects geochemical changes in source composition.

Generally, the Upper Ordovician samples all exhibit similar trace-element patterns when plotted on extended REE plots (Figure 1a). Most of the samples show a strong Nb depletion, relative enrichment in the light REE (LREE)

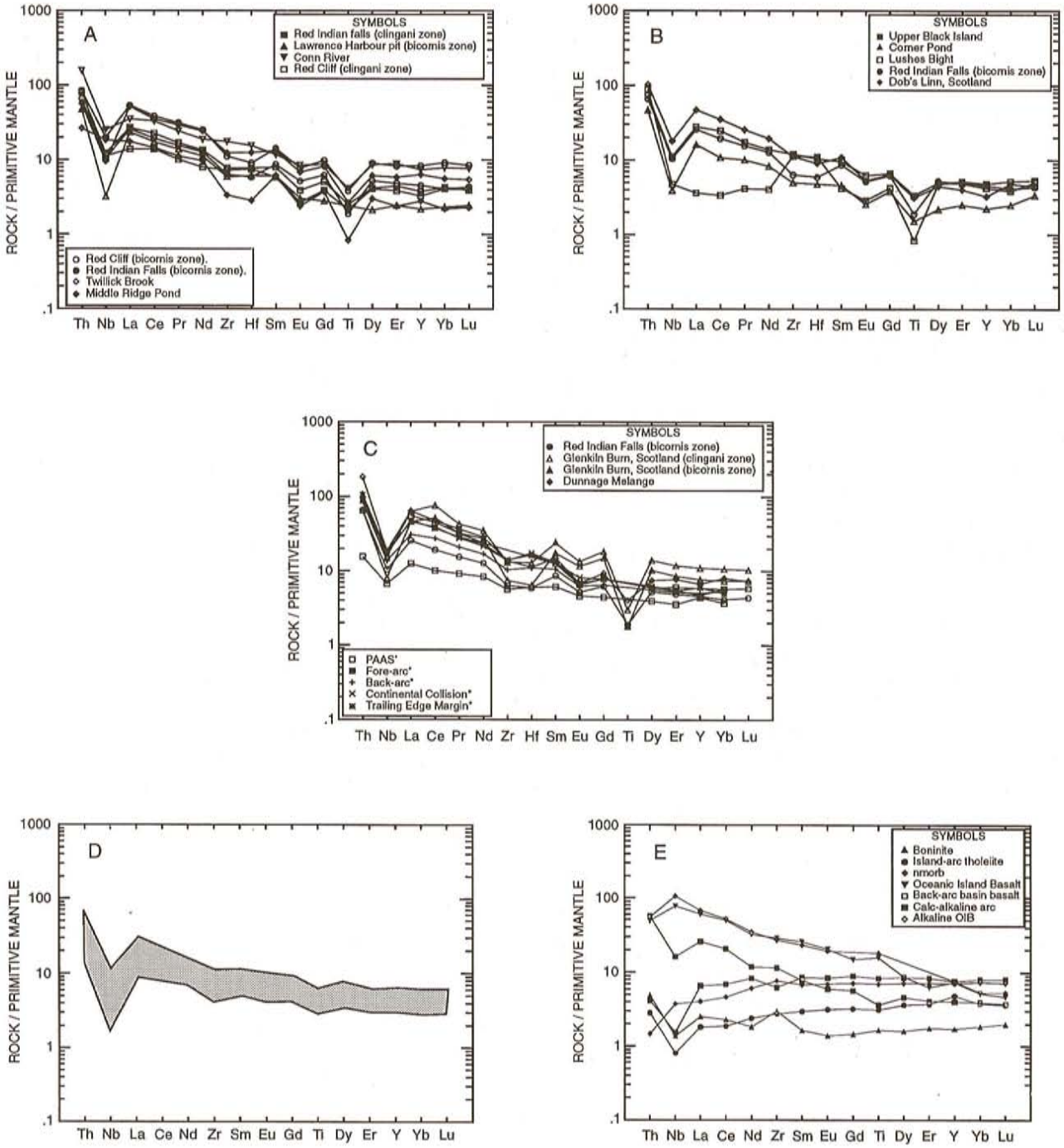

Figure 1. *Extended REE plots for various shale samples. A) Lawrence Harbour Formation shales and equivalents; B) various samples from Newfoundland and Scotland; C) Dunnage Melange and Glenkiln Burn, Scotland, samples plotted with a Lawrence Harbour shale for reference. (* from McLennan* et al., *1990) (+ from Taylor and McLennan, 1985); D) primitive mantle-normalized calc-alkaline volcanic rock pattern for Dunnage Zone volcanic rocks; E) primitive mantle-normalized patterns for volcanic rock types that could be contributing to the sedimentary basins.*

relative to the heavy REE (HREE), and a strong depletion in Zr, Hf, and Ti. All samples show negative Eu anomalies of varying magnitude.

There are also some differences among samples. The Lawrence Harbour pit specimen exhibits a more pronounced Nb depletion relative to the others. It is also depleted in HREE with respect to other Lawrence Harbour shale and equivalents. The Lush's Bight Group sample shows positive Zr and Hf relative to the REE's, and an overall depletion in the REE's, suggesting a dominant boninite input (Figure 1b). Samples from Glenkiln Burn Scotland (Figure 1c) have slight overall enrichment and similar extended REE patterns relative to the Lawrence Harbour samples. They also have more pronounced Ti, Zr, Hf, and Nb depletions. The matrix of unknown age from the Dunnage Melange is also geochemically similar to the Lawrence Harbour shales and follows similar trends on its extended REE plot (Figure 1c).

Also included in the plots are the values for Post-Archean Average Australian Shale or PAAS (Taylor and McLennan, 1985). These are plotted with Lawrence Harbour Formation results in Figure 1c. The PAAS extended REE plot is similar to those of the Lawrence Harbour shales, although there are no values for Th, Nb, Zr, Hf, or Ti, making it an incomplete comparison.

Several average values of turbiditic muds (McLennan *et al.*, 1990) from various locations world wide are also plotted as indicators of geochemical trends from differing tectonic settings (Figure 1c). The fore-arc (FA) samples show a small Nb depletion relative to the other specimens. The back-arc (BA) samples plot appear similar to the shales, with LREE enrichment and Nb depletion. Trailing edge (TE) samples show less of a Hf depletion relative to the shales and a less pronounced negative Eu anomaly. Strike-slip (SS), continental-arc (CA), and continental-collision (CC) environments all have similar extended REE plots to those of BA and TE samples. The CC plot showed Hf enrichment, as did CA samples, although to a lesser extent than CC. Aside from the FA sample, all extended REE plots of tectonic setting values follow similar trends of slight LREE enrichment and Nb depletion.

DISCUSSION

The data suggest several similarities in the geochemical signatures of the Lawrence Harbour Formation, the other Upper Ordovician shales of the Exploits Subzone, and the age-equivalent Scottish units. The overall trends resemble calc-alkaline distributions that are associated with mature (calc-alkaline) island-arcs (e.g., Swinden, 1991). The Zr, Hf, Ti, and Nb depletion (relative to the REE's) observed in some samples is often related to island-arc magmatism. Alternatively, it may also illustrate a heavy mineral affect caused by the fractionation of heavier minerals (zircon for Zr and Hf; magnetite for Ti) by sedimentary sorting processes (McLennan *et al.*, 1993). The proportion of this depletion due to an inherited island-arc magmatism signature, and that of heavy mineral effects is dependant on the detrital and pelagic components within the shales. The negative Eu anomalies observed in most samples are due to the fractionation of plagioclase feldspar into coarser sediment. The Nb depletion reflects the chemical signature of arc-related subduction-zone environments. As noted above, the Lawrence Harbour pit sample, with its strong Nb and HREE depletion, is slightly different relative to the other samples. However, there is a broad range of possible volcanic-arc patterns, and this sample is not so unusual.

In terms of the tectonic setting of the samples, the extended REE plots illustrate several trends. Figure 1d shows the range of mean values for Dunnage Zone calc-alkaline volcanic rocks of the Buchans–Roberts Arm groups. It is apparent that the trend defined for the calc-alkaline volcanic rocks is similar to those of the Lawrence Harbour Formation and equivalent units. The only marked difference observed is that some of the shales have a greater Zr and Ti depletion than the volcanic trends. This possibly reflects an enhancement of the island-arc signature by separating heavy mineral affect. The calc-alkaline arc signature of the shales becomes more apparent when the extended-REE patterns are compared with trends of volcanic rocks from differing tectonic settings (Figure 1e). The Th–La–Sc ternary diagram of (Figure 2) illustrates where the samples plot with respect to the values of both sediment from differing tectonic environments, and from differing source terranes. Samples from the Lawrence Harbour Formation plot within the oceanic island-arc (OIA) and continental island-arc (CIA) fields, nearest to BA and SS values of averaged turbiditic muds (McLennan *et al.*, 1990). There is a slight separation observed in the Th–La–Sc plots for the Upper Ordovician shales, but the significance of this trend is unclear. The Glenkiln Burn samples have slightly increased La values and plot near the TE environment, but are outside of the continental island-arc field. This suggests that there may be some difference in the geochemistry of the Scottish samples. The Dunnage Melange sample plotted within the CIA setting. Figure 2b illustrates the Th–La–Sc plots for shales of Early Ordovician and Early Silurian age. It is apparent that these samples are geochemically different from the Lawrence Harbour shale when both the extended REE and the ternary plots are examined.

CONCLUSIONS

This study is still at a preliminary stage, meaning that regional correlation, provenance, and tectonic setting inferences are speculative. Nevertheless, the trace and REE data of samples from the Lawrence Harbour Formation appear to suggest the following:

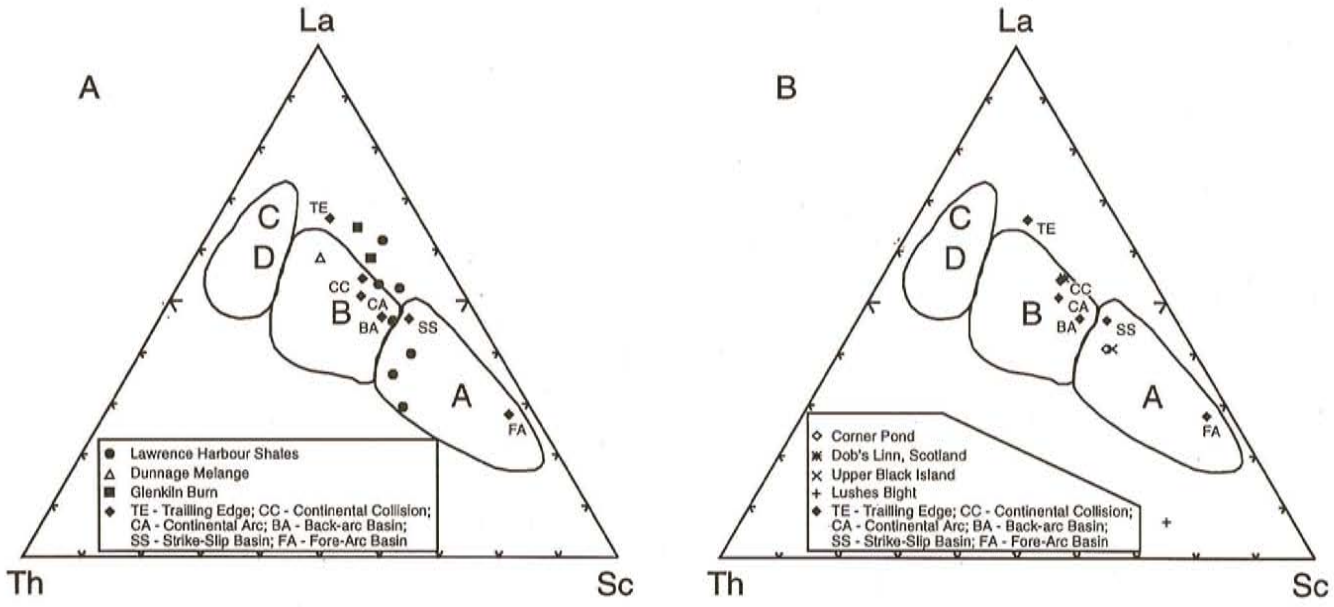

Figure 2. *Ternary plot of Th, La, and Sc with averaged data (McLennan* et al., *1990) from turbidites of varying tectonic setting. A) Lawrence Harbour shale; B) various samples from Newfoundland and Scotland. Fields are A – oceanic island-arc; B – continental island-arc; C – active continental margin; D – passive margin (after Rollinson, 1993).*

a) extended REE plots show marked similarities between samples from the Lawrence Harbour Formation and equivalent units,

b) there is no strong evidence of local influence from other potential volcanic source terranes,

c) the resemblance of the extended REE plots to calc-alkaline patterns and the Th–La–Sc diagrams indicate an island-arc (possibly back-arc) tectonic setting for the Lawrence Harbour Formation (the Glenkiln Burn samples may reflect some differences in source terrane compositions),

d) although the trends for Upper Ordovician shales cannot be considered unique, there does appear to be a consistent correlation between the geochemistry of the shales,

e) similarities between the Dunnage Melange sample of unknown age and the Upper Ordovician shale extended REE patterns suggest that further geochemical study may prove valuable in determining the age and origin of the matrix of that unit, and

f) Sm/Nd isotope analyses combined with the trace- and rare-earth elements results of additional samples, will assist in furthering attempts at fingerprinting of the Lawrence Harbour Formation.

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