

Late Diagenetic Trace Element Remobilization in Organic-Rich Black Shales of the Taconic Foreland Basin of Québec, Ontario and New York

by

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with 6 figures and 7 tables

Abstract: We report measured concentration values of 32 trace elements, including the fourteen rare earth elements (REE), in organic-rich black shales of the Late (Caradocian) Ordovician Utica Shale magnafacies of Québec, Ontario and New York by an inductively coupled plasma mass spectrometer (ICP-MS). We report these analyses for selected shale samples from the three localities. These representative samples have similar mineralogical composition and organic carbon content. The time correlative shale units are of different thermal grades: Québec (immature- T_{max} 20° to 50°C), Ontario (mature and oil-bearing- T_{max} - 50° to 140°C) and New York (post-mature- T_{max} greater than 200°C). The results show significant variation in trace element concentration (Sr, Th, U, Pb and the light and middle rare earth elements) with respect to the post-Archean Australian Shale (PAAS).

The PAAS-normalized trace element abundance patterns, but not individual element concentrations, of these shales are similar to PAAS including negative Nb and Ta anomalies. There is a progressive decrease in several trace element ratios (Th/U, Th/Pb, Nb/U, Ce/Pb and Ce/Yb) with increasing thermal maturity, indicating that, during late diagenesis, there is light rare earth element (LREE) and Th depletion and U-enrichment. The trace element ratios of the immature samples are similar to NASC and PAAS values. The detailed results, however, suggest that U, Th, Pb and some of the REE mobilize during diagenesis. For example, $(La/Sm)_N$ and $(La/Yb)_N$ show progressive light REE (LREE) depletion with increasing thermal grade. The PAAS-normalized REE patterns of these shales show distinct differences such as a characteristic light REE depletion (Σ LREE average: 57 ppm) with increasing thermal grade. We relate the characteristic LREE depletion observed in these shales to the extent of burial diagenesis. The results of this study indicate that trace elements, particularly the LREE, U, Pb and Th can be remobilized during diagenesis. The trace elements migrate from the shales into the pore waters during or subsequent to illitization and related decomposition of organic matter. Those elements most affected by this "interstitial diffusion" such as the LREEs show characteristic depletions attributable to this process.

Introduction

Trace element concentrations in sediments reflect a combination of competing influences such as provenance, weathering, diagenesis, sediment sorting and the aqueous geochemistry of the specific elements. Most trace element geochemical studies concentrate on clay-rich lithologies because they contain the highest concentrations of the trace elements, including the REE. The trace element abundances in clay-rich lithologies are particularly useful in provenance studies. It is possible to identify particular geochemical processes using selected trace elements with characteristic geochemical affinities. Trace element and REE abundance patterns in sedimentary rocks are useful provenance indicators (eg. Taylor and McLennan, 1985; Basu et al., 1990). The REE abundance patterns may also be useful in assessing paleoredox conditions and depositional environments (Schijf et al., 1991; Murray et al., 1992; Nath et al., 1992). The chondrite-normalized trace element and REE

abundance patterns of post-Archean sediments from intermediate to granitoid continental sources are generally uniform and are characterized by negative Nb and Ta anomalies, enrichment in light rare earth elements (LREE; La to Nd), negative Eu-anomalies, and flat middle (MREE; Sm to Ho) and heavy rare earth element (HREE; Er to Lu) abundance patterns (Taylor and McLennan, 1985; McLennan, 1989; Rollinson, 1993). The post-Archean Australian Shale composite (PAAS- Nance and Taylor, 1976) approximates trace element and REE abundance patterns of sediments derived from the upper continental crust. The REE's in particular, as well as several other trace elements, may be mobile under specific weathering conditions (Condie, 1993; McDaniel et al., 1994; Condie et al., 1995). Recent work suggests that mobilization or fractionation of the REEs in shales occurs during sedimentation and diagenesis (Schieber, 1988; Awwiller and Mack, 1991; Condie, 1993; Awwiller, 1994). There is also evidence for localized trace element and REE mobility during early diagenesis in intermittently active tectonic settings (Milodowski and Zalasiewicz, 1993; Bock et al., 1994). Release of trace elements and REEs occurs by the breakdown of unstable minerals during early diagenesis. These elements are subsequently complexed in organic-rich layers by authigenic clays and/or phosphates (Awwiller, 1993; Kidder and Eddy-Dilek, 1994).

The purpose of this paper is to characterize the trace element and REE abundance patterns of Late Ordovician organic-rich black shales, specifically the Utica Shale magnafacies of the Taconic foreland basin of North America. We also examine the relationship between certain trace elements and the effects of late diagenetic processes (eg. catagenesis- oil formation). The data presented here contributes to a broad geochemical characterization of Late Ordovician black shales. The geochemical characterization of Late Ordovician shales, in particular the Utica Shale magnafacies of Québec, Ontario and New York, is important for several reasons. The extent of burial diagenesis in each of the three regions is variable. Deposition of these organic-rich shales predates the development of terrestrial biotas (Seilacher and Westphal, 1978; Edwards and Burgess, 1990). The occurrence of pandemic and endemic graptolite species, differences in benthic faunal diversity, reactivity of the entirely marine organic matter, the abundance of sulfides, overall similarity in mineralogy and the periodic lack of oxygen in the sediments contribute to some paleontological and geochemical characteristics unique to the Ordovician and to these black shales in particular.

Geologic and Stratigraphic Relationships

The Utica Shale magnafacies represents the earliest siliciclastic strata of the Taconic foreland basin (Lehmann et al., 1995). These organic-rich shales are part of a nearly continuous belt that extends from eastern North America westward into the continental interior. The magnafacies in Québec, Ontario and New York (Figs. 1 and 2) includes at least five unconformity-and/or condensed interval bounded units (Baird et al., 1992; Lehmann et al., 1995). Each unit records a pulse of foreland basin deepening and partial filling. Paleocurrent data indicate that deposition of silt-poor, organic-rich mud occurred on a subsiding ramp sloping eastward toward the siliciclastic sediment source (Fig. 1b). Thus, the black shales do not necessarily represent the deepest part of the basin; the deepest portion of this basin contains coarse grained, axial submarine fan deposits (Lehmann et al., 1995). Graptolite biostratigraphy (Ruedemann, 1925; Riva, 1969; Clark, 1972; Belt et al., 1979), bentonite stratigraphy (Delano et al., 1994; Goldman et al., 1994; Samson et al., 1995), and event and sequence stratigraphy (Baird et al., 1992; Baird and Brett, 1994; Baird et al., 1994; Hannigan et al., 1997) constrain the Utica Shale magnafacies in time.

The Lachine and L'otbiniere ('Utica') shales of southern Québec (Figs. 1 a and 2) range in age from *Orthograptus ruedemannii* to upper *Geniculograptus pygmæus* graptolite zones (Clark, 1972). These shales are black to very dark brown, chocolate brown-weathering, massive to thin bedded

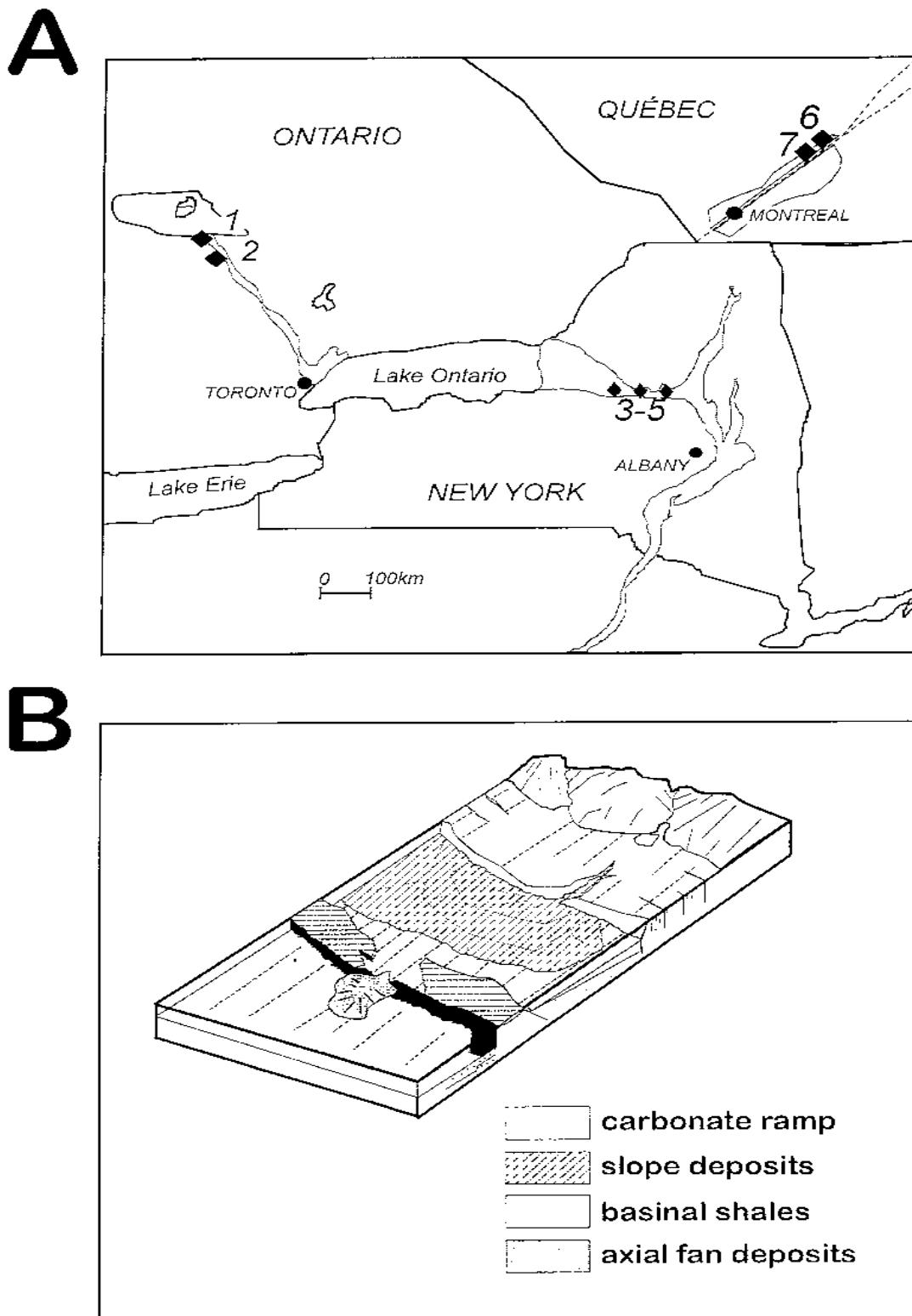


Fig. 1: A. Distribution of the Caradocian Taconic foreland basin black shales in Québec, Ontario and New York. Sample localities used in this study include: 1-Craigleath (Georgian Bay); 2-Bowmanville Quarry; 3-Nowadaga Creek; 4-Flat Creek; 5-Yatesville Creek; 6- L'egare Hotel section and 7-'Dona Cona' creek. B. Schematic representation of the Taconic foreland basin showing the spatial relationships of the carbonate ramp, basinal shales and axial fan deposits.

shales that display a brown streak, and an odor of petroleum when freshly broken. Unlike some of the correlative shale units of Ontario and New York, these shales are not carbonate-rich. The black

shales of Québec contain diagenetic and syngenetic pyrite (Belt et al., 1979; Hannigan and Mitchell, 1994) and are initially mature (oil prone) with an average organic carbon content of 5 wt. % (Heroux et al., 1979; Hannigan, 1993). Carbon-iron-sulfur systematics of these shales suggest an episodically anoxic-nonsulfidic depositional environment (Hannigan and Mitchell, 1994). The clay mineralogy of these shales is dominantly smectitic illite-smectite (I/S) (Bertrand et al., 1983).

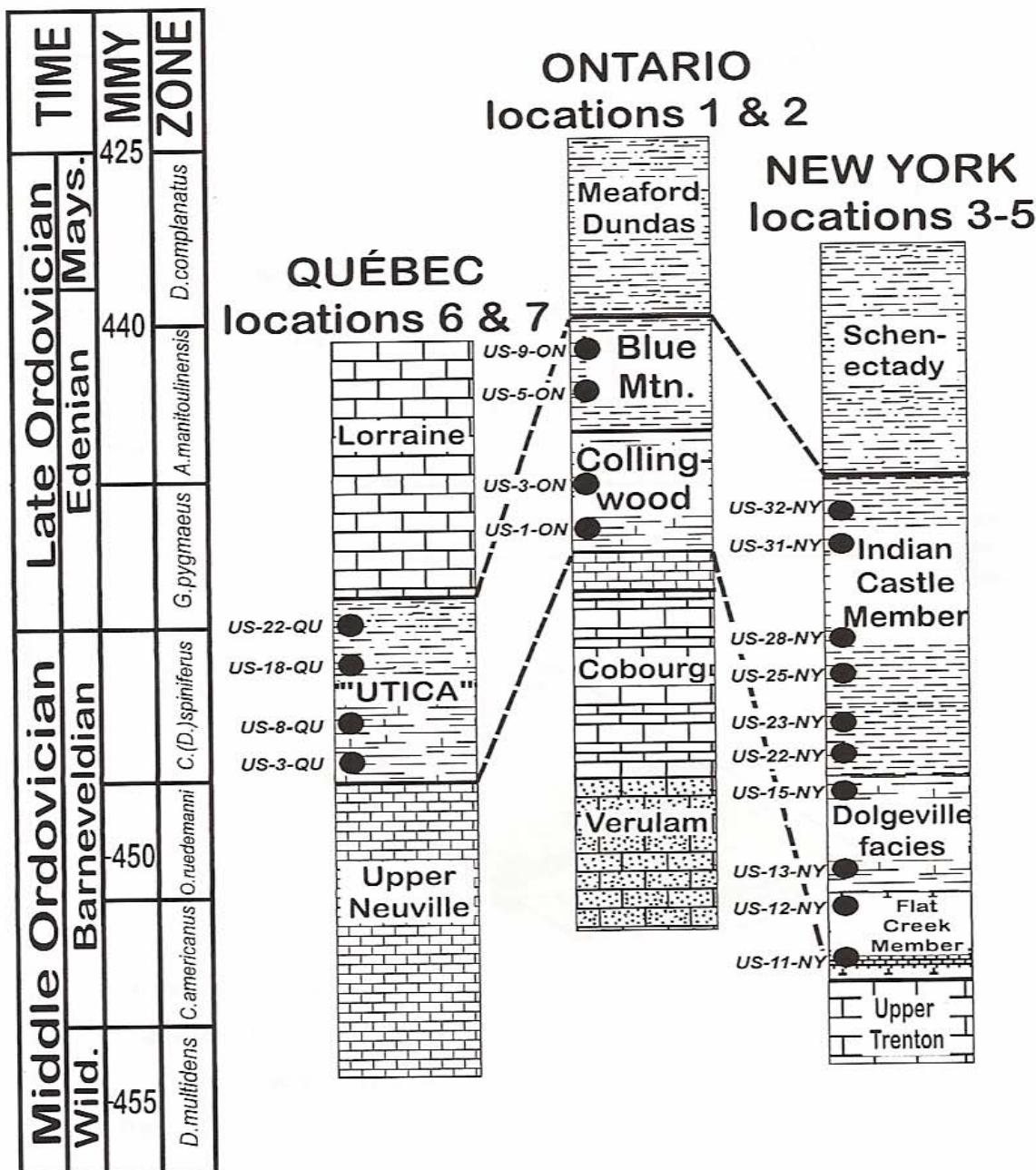


Fig. 2: Generalized Ordovician stratigraphy of Québec, Ontario and New York showing the biostratigraphic position of the samples used in this study. We note the samples analyzed in this study to the left of the respective stratigraphic column.

The Collingwood (Whitby) and Blue Mountain shales of Ontario (Figs. 1A and 2) are often carbonate-rich (up to 45 wt. %) and contain on average 5 wt. % organic carbon (Barker et al., 1990), although organic content is variable. These shale units have reached a marginal thermal maturation level with bitumen as a significant component of the organic matter. They range in age from *G.pygmaeus* to *Amplexograptus manitoulinensis* (Belt et al., 1979). Carbon-iron-sulfur systematics

these shales suggest deposition in a normal marine, episodically oxygen deficient environment. The Ontario shales contain primarily diagenetic pyrite with minor amounts of syngenetic pyrite (Baird et al., 1994). The clay mineralogy of these shales is dominantly illitic I/S (Macauley et al., 1983).

In New York (Figs. 1 a and 2), the Flat Creek-Dolgeville-Indian Castle shales are post-mature and are potential natural gas sources (Wallace and Roen, 1989). These units range in age from *Corynoides americanus* to *G.pygmaeus* (Ruedemann, 1925; Riva, 1969). Chronostratigraphy (Goldman et al., 1994; Delano et al., 1994; Samson et al., 1995) also constrains these units in time. The shales are often carbonate-rich (12 % to 45 wt. %) and contain varying amounts of organic carbon (2 % to 15 wt. %; Hannigan, 1993). Decreasing proportions of organic carbon in the eastern portion of the outcrop belt may not represent a decrease in organic matter flux to the sediments but rather the loss of volatile organics during catagenesis (Wallace and Roen, 1989). The C-S-Fe systematics and the type of pyrite (primarily diagenetic) of the Utica Shale magnafacies in New York suggest normal marine to poikiloaerobic depositional conditions (Hannigan, 1993). The clay mineralogy is dominantly illitic I/S with minor chlorite (Turner, 1985).

The relative abundance of minerals in the Utica Shale magnafacies varies depending on location within the basin. This is particularly evident in the 0.5 μm clay fractions. The majority of the variability relates to the extent of diagenesis as late diagenetic minerals such as pyrite and chlorite are more abundant in the New York samples (post-mature). Upon characterization of the mineralogy of the selected samples we chose samples with similar mineralogical composition for trace element analysis.

Analytical Methods

We analyzed the trace element and the REEs of the whole-rock shale samples with a VG Quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Union College facility in Schenectady, New York. We digested 50 mg of sample completely with 1 mL concentrated HNO_3 and 3 mL concentrated HF in a tightly sealed 15 mL Teflon TFE screw-cap bomb by heating on a hot plate for 24 hrs. After evaporating to dryness under lamps, we added 0.5 mL 2N HClO_4 and heated the samples to extreme dryness until the fuming ceased. We followed this with two successive 1 mL concentrated HNO_3 treatments (also heating to dryness). We prepared the final solutions by adding precisely 1 mL of the internal standard and diluting the sample to 100 mL with double distilled water. The composition of the internal standard was a 10 ppm solution of Ga, In, Cs, Bi and Re to correct instrumental drift for the ICP-MS analyses. We performed all sample preparation in the Class 100 clean room at the University of Rochester; all acids were ultra-pure.

Analytical Uncertainty

Analytical precision is often $< 2\%$ of the reported concentration of the individual elements in Table 1. Precision of the analyses, as determined from duplicate analyses of the samples beginning with the original powder weighing, is generally $< 5\%$ for the REEs and $< 10\%$ for the other trace elements. We also used two standards to determine the internal and external precision of the analyses. We analyzed BCR-1 (U.S. Geological Survey basalt rock standard) with its known concentration of the 32 trace elements. We compared our measured values to those from the literature (Table 1) to determine an external precision $< 2\%$. We measured another rock standard (USGS obsidian rock standard, NBS-287) to estimate the accuracy of the analytical procedure. We chose the BCR-1 and NBS-287 standards because the concentration of the trace elements are known and our previous work supports the use of the standards in retaining accuracy and maintaining precision in our analyses.

Table 1: Trace element and REE abundances of the Utica Shale magnafacies compared with BCR-1, chondrite and PAAS.

SAMPLE	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pr	Nd	Sm
US-3-QU	55.7	1348.9	11.1	50.7	6.8	198.4	15.34	30.28	3.39	12.69	2.26
US-8-QU	79.9	1963.5	19.9	59.3	7.4	180.1	20.64	40.43	4.78	18.46	3.40
US-18-QU	85.8	2243.4	21.9	69.8	8.2	236.2	20.97	40.78	4.75	18.71	3.47
US-22-QU	99.4	2339.5	23.1	70.0	8.7	282.0	22.73	43.56	5.10	19.53	3.54
US-I-ON	31.9	789.2	13.9	24.6	4.8	44.4	9.03	20.30	2.44	9.33	1.75
US-3-ON	87.6	1137.1	27.6	82.3	10.0	127.8	14.61	31.63	3.71	14.20	2.86
US-5-ON	83.1	1200.4	33.8	81.6	8.7	151.5	18.61	40.69	4.60	17.66	3.62
US-9-ON	92.0	921.4	24.3	89.5	8.7	180.8	13.48	29.61	3.49	13.36	2.71
US-11-NY	31.3	1302.7	12.3	58.3	3.4	108.6	4.78	12.68	1.74	7.41	1.78
US-12-NY	178.9	41.2	6.7	213.1	17.1	232.7	3.31	8.98	1.23	5.19	1.21
US-13-NY	26.2	1224.3	12.3	58.3	3.4	87.4	5.13	12.68	1.66	7.00	1.58
US-15-NY	23.2	1733.9	9.2	29.4	2.0	95.4	2.63	6.65	0.93	3.94	0.95
US-22-NY	82.7	432.1	27.7	86.1	8.9	259.2	16.97	41.03	5.40	22.49	4.99
US-23-NY	37.9	1100.8	15.7	62.3	4.6	113.2	11.74	28.02	3.61	14.12	3.14
US-25-NY	96.2	559.3	29.5	89.8	9.3	250.5	12.88	31.12	3.98	16.79	3.96
US-28-NY	40.6	1833.0	18.7	48.2	4.2	330.6	9.55	22.03	2.95	12.17	2.81
US-31-NY	96.1	103.3	17.9	71.8	11.7	389.7	15.13	36.57	4.67	19.73	4.66
US-32-NY	193.2	69.7	20.2	142.4	17.7	440.8	6.91	17.50	2.29	9.66	2.13
BCR-1 ^a	47.00	330.00	39.00	185.00	13.40	678.00	25.00	53.60	6.90	28.60	6.55
Chondrite ^b	2.30	7.25	1.57	3.82	0.24	2.41	0.24	0.61	0.09	0.46	0.15
PAAS ^c	160.00	200.00	27.00	210.00	19.00	650.00	38.20	80.00	8.83	33.90	5.55

NOTE: f_{SmNd} is calculated as: $[(^{147}\text{Sm}/^{144}\text{Nd})/0.1967]^{-1}$ Ce/Ce^* is calculated as: $(\text{Ce}_{\text{sample}}/\text{Ce}_{\text{shale}})/\text{Ce}^*$, where Ce^* is a linear interpolation between shale-normalized La and Pr values Eu/Eu^* is calculated as: $(\text{Eu}_{\text{sample}}/\text{Eu}_{\text{shale}})/\text{Eu}^*$, where Eu^* is a linear interpolation between shale-normalized Sm and Tb values

Table 1. (continued)

Sample	<i>Eu</i>	<i>Cld</i>	<i>Tb</i>	<i>Dy</i>	<i>Ho</i>	<i>Er</i>	<i>Tm</i>	<i>Yb</i>	<i>Lu</i>	<i>Hf</i>	<i>Ta</i>	<i>Pb</i>
<i>US-3-QU</i>	0.45	1.86	0.28	1.50	0.31	0.86	0.12	0.82	0.13	1.28	0.10	8.30
<i>US-8-QU</i>	0.68	2.83	0.42	2.30	0.47	1.32	0.17	1.18	0.18	1.35	0.25	7.19
<i>US-18-QU</i>	0.70	2.81	0.44	2.33	0.47	1.31	0.17	1.18	0.18	1.47	0.25	8.58
<i>US-22-QU</i>	0.71	2.97	0.45	2.33	0.48	1.36	0.18	1.22	0.19	1.49	0.28	19.20
<i>US-1-ON</i>	0.34	1.70	0.28	1.63	0.36	1.05	0.14	1.01	0.15	0.62	0.12	14.29
<i>US-3-ON</i>	0.60	3.23	0.55	3.22	0.73	2.12	0.29	2.05	0.31	1.89	0.27	18.80
<i>US-5-ON</i>	0.74	3.86	0.63	3.58	0.81	2.41	0.33	2.30	0.35	1.94	0.24	17.70
<i>US-9-ON</i>	0.56	2.98	0.52	2.95	0.67	1.94	0.27	1.88	0.29	2.28	0.26	16.90
<i>US-11-NY</i>	0.36	1.67	0.29	1.71	0.39	1.05	0.14	0.90	0.14	1.72	0.55	14.25
<i>US-12-NY</i>	0.29	1.39	0.23	1.30	0.30	0.86	0.12	0.79	0.12	3.99	0.54	12.53
<i>US-13-NY</i>	0.33	1.52	0.27	1.56	0.35	0.96	0.13	0.91	0.14	1.32	0.13	11.80
<i>US-15-NY</i>	0.24	1.13	0.18	1.06	0.23	0.68	0.09	0.62	0.10	0.77	0.04	12.19
<i>US-22-NY</i>	1.01	4.70	0.76	4.43	1.02	2.64	0.37	2.57	0.40	2.62	0.04	11.33
<i>US-23-NY</i>	0.64	2.88	0.47	3.04	0.69	2.01	0.28	1.89	0.29	1.94	0.04	11.02
<i>US-25-NY</i>	0.83	3.82	0.61	3.75	0.83	2.36	0.33	2.33	0.35	2.57	0.07	11.62
<i>US-28-NY</i>	0.58	2.77	0.45	2.90	0.61	1.71	0.23	1.64	0.25	1.52	0.07	17.54
<i>US-31-NY</i>	0.96	4.39	0.69	4.20	0.95	2.83	0.38	2.70	0.42	3.08	0.12	21.39
<i>US-32-NY</i>	0.46	2.00	0.35	1.97	0.44	1.20	0.16	1.06	0.16	3.04	0.43	17.38
<i>BCR-I^a</i>	1.92	6.82	1.05	6.37	1.34	3.71	0.55	3.39	0.50	4.90	0.79	13.56
<i>Chondrite^b</i>	0.06	0.20	0.04	0.25	0.05	0.16	0.02	0.16	0.02	0.10	0.01	0.02
<i>PAAS^c</i>	1.08	4.66	0.77	4.68	0.99	2.85	0.41	2.82	0.43	5.00	0.31	18.00

^a BCR-I values: U, Th, Pb from Tatsumoto *et al.* (1972); other trace and REE from Potts *et al.* (1987)^b Chondrite values from McDonough and Sun (1995)^c PAAS values from Nance and Taylor (1976); Taylor and McLennan (1985); McLennan (1989)

Table 1. (cont'd)

SAMPLE	Th	U	fSm/Nd	Ce/Ce*	Eu/Eu*	$\Sigma LREE$	ΣREE
US-3-QU	4.54	1.37	-0.45	0.91	1.63	61.7	70.3
US-8-QU	5.80	2.19	-0.44	0.89	1.64	84.3	97.3
US-18-QU	5.87	2.56	-0.43	0.89	1.64	85.2	98.3
US-22-QU	6.54	1.81	-0.44	0.88	1.62	90.9	104.3
US-I-ON	2.27	1.10	-0.42	0.94	1.53	41.1	49.5
US-3-ON	6.14	5.28	-0.38	0.94	1.61	64.1	80.1
US-5-ON	6.11	3.62	-0.37	0.96	1.59	81.6	100.2
US-9-ON	7.47	4.11	-0.38	0.94	1.60	59.9	74.7
US-11-NY	2.46	1.43	-0.27	0.94	1.62	26.6	35.0
US-12-NY	2.29	2.91	-0.29	0.95	1.85	18.7	25.3
US-13-NY	2.19	1.23	-0.31	0.94	1.65	26.5	34.2
US-15-NY	1.72	1.16	-0.26	0.91	1.90	14.2	19.4
US-22-NY	7.36	5.62	-0.32	0.93	1.61	85.9	108.8
US-23-NY	3.95	3.79	-0.32	0.93	1.62	57.5	72.8
US-25-NY	7.66	6.06	-0.28	0.94	1.68	64.8	83.9
US-28-NY	3.86	4.41	-0.29	0.90	1.63	46.7	60.6
US-31-NY	6.89	4.69	-0.28	0.94	1.65	76.1	98.3
US-32-NY	5.98	4.85	-0.33	0.95	1.70	36.4	46.3
BCR-1 ^a	5.99	1.73	-0.30	0.89	2.32	114.1	146.3
Chondrite ^b	0.03	0.01	-0.01	0.88	2.81	1.4	2.5
PAAS ^c	14.60	3.10	-0.46	0.95	1.00	160.9	185.2

All sample concentrations reported in Table 1 are blank corrected for laboratory procedures. We found the published NBS-287 values for the trace elements and the REE concentrations to be within 2 to 5 % of the analyzed results by our ICP-MS method using BCR-1 as the standard. Thus, we are confident our analyses of 18 shales as reported in Table 1 have an overall precision and accuracy better than 5 %. In our opinion, as digestion of the samples was complete, we suspect that accessory phases such as monazite and xenotime, if present, were in solution.

We report the analyzed gadolinium concentration knowing that systematically higher concentrations, though not noted in our study, could suggest interferences on ^{157}Gd from $^{138}\text{BaF}^+$ or $^{140}\text{CeOH}^{++}$. For examination of HREE depletion and LREE depletion, we take Sm as the middle REE (MREE) marker because of possible Gd mass interference and because Eu has multiple oxidation states. We measured the ^{139}La and ^{141}Pr masses because we used dilute (2N) HClO_4 evaporated to repeated dryness and so expect no CaClO_4 or MgClO_4 interferences (Longerich, 1993). We do not, however, report chromium and vanadium concentrations due to possible molecular interferences and other analytical problems (eg. ^{35}ClO). We could not compare germanium internally because it volatilizes with Si during HF evaporation.

Mineralogy

We determined, semi-quantitatively, the mineralogy of the whole-rock shale samples and 0.5 μm -size clay fractions both optically (modal analyses of high quality polished thin sections) and by x-ray diffraction (XRD) using the Scintag 2000 X-ray Diffractometer facility at the University of Rochester. We examined the samples for heavy minerals optically before and after heavy liquid separation. Tables 2 and 3 show the whole-rock mineralogical data and the mineralogical data for the 0.5 μm clay fraction, respectively.

Table 2: Whole-rock mineral abundances* (in wt.%)

<i>SAMPLE</i>	<i>Quartz</i>	<i>K-feldspar</i>	<i>Plagioclase</i>	<i>Calcite</i>	<i>Biotite</i>	<i>Clay</i>
<i>US-3-QU</i>	14	2	0	14	1	69
<i>US-8-QU</i>	16	1	1	13	1	68
<i>US-18-QU</i>	14	2	0	14	0	70
<i>US-22-QU</i>	15	1	1	12	1	70
<i>US-1-ON</i>	9	2	1	15	1	72
<i>US-3-ON</i>	12	0	0	15	0	73
<i>US-5-ON</i>	11	0	1	13	1	74
<i>US-9-ON</i>	10	2	1	15	0	72
<i>US-11-NY</i>	9	0	1	11	2	77
<i>US-12-NY</i>	8	0	1	11	2	78
<i>US-13-NY</i>	9	0	1	12	1	77
<i>US-15-NY</i>	9	0	1	10	2	78
<i>US-22-NY</i>	9	1	0	10	1	79
<i>US-23-NY</i>	11	1	1	9	1	77
<i>US-25-NY</i>	8	1	0	10	2	79
<i>US-28-NY</i>	9	0	1	10	2	78
<i>US-31-NY</i>	10	0	1	8	1	80
<i>US-32-NY</i>	9	0	1	10	2	78

* Estimated to be accurate to approximately 10% of the relative abundance

Table 3: Mineral abundances* (in wt.%) and I/S expandability in the <0.5 µm clay fraction

SAMPLE	Kaolinite	Illite	I/S	Chlorite	% Illite in I/S
US-3-QU	2	2	95	0	25
US-8-QU	2	3	94	0	22
US-18-QU	3	1	92	0	22
US-22-QU	5	0	91	0	21
US-1-ON	2	22	76	0	35
US-3-ON	1	25	74	0	42
US-5-ON	2	29	68	0	44
US-9-ON	2	31	66	1	41
US-11-NY	1	42	44	10	87
US-12-NY	0	54	37	9	88
US-13-NY	1	53	36	10	85
US-15-NY	Tr.	56	33	11	86
US-22-NY	1	58	30	10	87
US-23-NY	0	64	26	9	88
US-25-NY	0	55	34	11	89
US-28-NY	0	60	30	10	90
US-31-NY	1	69	18	12	88
US-32-NY	0	61	26	13	87

* Estimated to be accurate to approximately 10% of the relative abundance

Low Temperature Geochemical Data

Previous analyses of the samples used in our current study provide organic carbon (LECO Carbon Analyzer, before and after ashing at 450°C; Hannigan, 1993) and carbonate contents (derived from measured carbon values). The previous study also included data for reactive iron and pyritic sulfur content using HCl digestion and chromium reduction (for detailed procedures see Hannigan, 1993). Table 4 contains these data for the samples used in our current study.

Results

We compare our trace element and REE abundance patterns to accepted post-Archean Australian Shale (PAAS) composite values (Taylor and McLennan, 1985; McLennan, 1989). We use PAAS because we know the locality of each of the samples as well as the specific sedimentary rock types used to compile the standard. Samples used to compile the PAAS standard are from drill core and the trace element abundances for PAAS represent an average of 23 individual analyses (Nance and Taylor, 1976). PAAS is an average of shales covering extensive areas of unmetamorphosed upper crust. We prefer the PAAS standard over the NASC to examine the REE abundance patterns in the present study simply because much more is known about each of the shales of the PAAS standard.

The PAAS-normalized trace element patterns for the Utica Shale magnafacies samples (Fig. 5) show variations in the abundances of the elements including positive and negative anomalies of Sr that reflect the carbonate control of this element in the shales. There is, however, no correlation observed between the carbonate content and Sr concentration in these samples. As only three of the New York samples show a negative Sr anomaly when normalized to chondrite and, due to the scatter of these samples throughout the stratigraphic column, we discount the influence of feldspar removal from the source rock prior to weathering on the Sr abundance in these shales. The decrease

Table 4: Carbon and iron geochemical data (in wt.%) for samples used in the current study (data from Hannigan 1993).

SAMPLE	Organic Carbon	Carbonate Carbon*	Total Carbon	Reactive Iron	Pyritic Iron**	Total Iron	Degree of Pyritization***
US-3-QU	3.92	14.47	5.66	0.53	1.24	1.60	0.67
US-8-QU	4.05	13.98	5.73	0.24	1.24	1.48	0.84
US-18-QU	3.47	13.12	5.05	0.35	1.07	1.42	0.75
US-22-QU	3.57	13.57	5.20	0.47	1.24	1.71	0.73
US-1-ON	3.67	19.22	5.98	0.58	1.37	1.95	0.70
US-3-ON	3.53	19.87	5.92	0.54	1.43	1.97	0.73
US-5-ON	3.68	19.85	6.06	0.59	1.50	2.09	0.72
US-9-ON	3.87	19.00	6.15	0.53	1.30	1.83	0.71
US-11-NY	4.60	15.60	6.47	0.37	1.54	1.91	0.81
US-12-NY	4.50	16.10	6.43	0.34	1.27	1.61	0.79
US-13-NY	4.76	14.27	6.47	0.55	1.29	1.84	0.70
US-15-NY	4.99	12.27	6.46	0.65	1.40	2.05	0.68
US-22-NY	4.21	12.86	5.75	0.67	1.14	1.81	0.63
US-23-NY	4.30	15.51	6.16	0.63	1.36	1.99	0.68
US-25-NY	4.27	15.30	6.11	0.60	1.41	2.01	0.70
US-28-NY	5.09	17.80	7.23	0.48	1.36	1.84	0.74
US-31-NY	4.59	14.59	6.34	0.41	1.47	1.88	0.78
US-32-NY	4.97	17.31	7.05	0.43	1.55	1.98	0.78

* carbonate carbon = $8.33 \times \text{wt.\% inorganic carbon}$ ** pyritic iron = $0.871 \times \text{wt.\% pyritic sulfur}$

*** degree of pyritization (DOP) = pyritic iron / (reactive iron + pyritic iron)

in Sr concentration from Québec to New York could, however, be due to plagioclase breakdown and removal of Sr from the system during early diagenesis. Several of these samples also show Nb and Ta anomalies that are, in the case of Nb, significantly lower than the anomalies of PAAS. The Nb-Ta anomalies suggest a continental crust source, not an arc-derived source as suggested by Anderson and Samson (1995). The trace element abundance patterns show that samples from the three regions of the foreland basin are significantly dissimilar. We assessed the degree of dissimilarity in trace element abundances using a statistical dissimilarity measure. Dissimilarity measures (Davis,

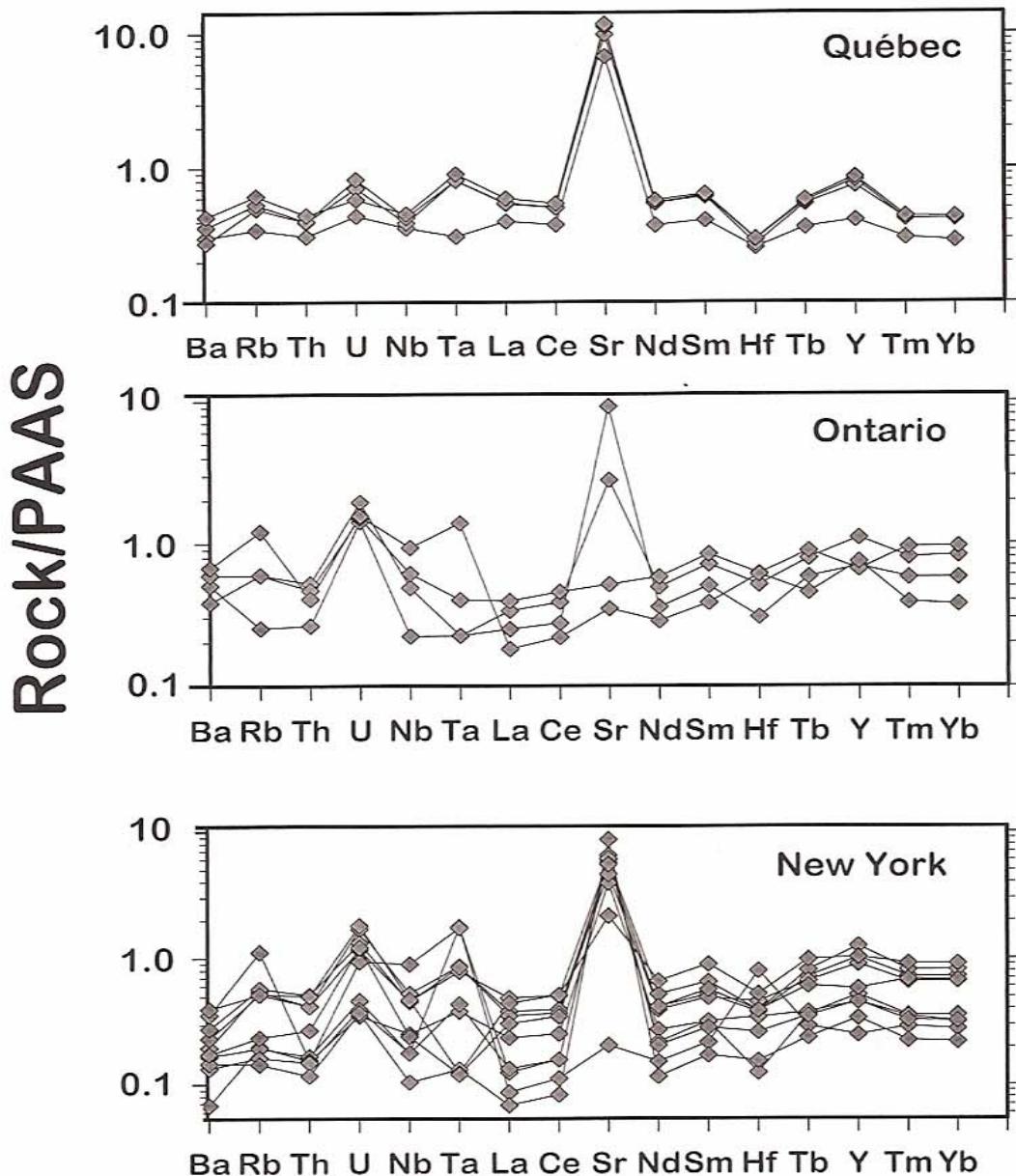


Fig. 3: PAAS-normalized trace element patterns for the Utica Shale magnafacies. We observe some carbonate control on Sr concentration despite the fact that the samples analyzed in our study contain less than 15 wt. % carbonate. The Nb and Ta concentrations are significantly lower than in PAAS implying continental crustal sources for the siliciclastics.

1986) estimate the distance or unlikeness of two cases (samples). A large dissimilarity value indicates that two cases are far apart. Table 5 shows the rescaled Euclidean distances between each of the samples in our study using the trace element part per million concentration data for all elements analyzed. Standardization of these values is to a range of zero to one. Euclidean distance is an analogue in N-dimensional space of the linear distance between two points in 2 or 3-dimensions. This statistic equals the sum of the squares of differences of the N variable values between two points. For each dissimilarity coefficient for the variable being standardized, the procedure subtracts the minimum value and then divided by the range. All variables have a value of 0.50, if the range is zero. The relatively homogeneous trace-element composition of the shales within each of the three individual regions studied supports other evidence that the dominant siliciclastic source of all three regions at the time of Utica Shale deposition was Grenville basement (or recycled sediments derived from Grenville basement; Wynne-Edwards, 1972; Dickin et al., 1990; Marcantonio et al.,

1990; Daly and McLelland, 1991; Lehmann et al., 1995). Andersen and Samson (1995) suggested, based on Sm-Nd isotope systematics, that sediment derived from uplifted Grenville crust dominated the provenance of the Utica Shale magnafacies in New York.

Table 3. Residual Euclidean Dissimilarity (Rescaled from 0 to +1).

SAMPLE	US-3-QU	US-8-QU	US-18-QU	US-22-QU	US-1-ON	US-3-ON	US-5-ON	US-9-ON	US-11-NY	US-12-NY	US-13-NY
US-3-QU	----	0.0253	0.0176	0.0090	0.0388	0.0301	0.0235	0.0510	0.0326	0.9573	0.0397
US-8-QU	0.0253	----	0.0008	0.0097	0.0157	0.0295	0.0253	0.0744	0.0091	0.9770	0.0136
US-18-QU	0.0176	0.0008	----	0.0022	0.0233	0.0285	0.0274	0.0692	0.0114	0.9731	0.0177
US-22-QU	0.0090	0.0097	0.0022	----	0.0313	0.0271	0.0240	0.0622	0.0313	0.9676	0.0261
US-1-ON	0.0157	0.0233	0.0313	----	0.0388	0.0425	0.0898	0.3424	0.9879	0.0139	0.0383
US-3-ON	0.0388	0.0157	0.0285	0.0271	0.0388	----	0.0034	0.0456	0.0346	0.9481	0.0410
US-5-ON	0.0388	0.0301	0.0274	0.0240	0.0425	0.0034	----	0.0405	0.0364	0.9470	0.0855
US-9-ON	0.0510	0.0744	0.0692	0.0622	0.0898	0.0456	0.0405	----	0.0800	0.9089	0.0000
US-11-NY	0.0326	0.0091	0.0114	0.0313	0.3424	0.0346	0.0364	0.0800	----	0.9796	0.9832
US-12-NY	0.9573	0.9770	0.9731	0.9676	0.9879	0.9481	0.9470	0.9089	0.9796	----	0.9668
US-13-NY	0.0397	0.0136	0.0177	0.0261	0.0139	0.0383	0.0410	0.0855	0.0000	0.9832	0.0161
US-15-NY	0.0517	0.0231	0.0281	0.0366	0.0180	0.0559	0.0584	0.1029	0.0172	1.0000	0.2429
US-22-NY	0.2946	0.3249	0.3183	0.3098	0.3424	0.3003	0.2937	0.2478	0.0192	0.7549	0.0576
US-23-NY	0.0216	0.0108	0.0094	0.0128	0.0243	0.0206	0.0199	0.0640	0.0114	0.9561	0.0576
US-25-NY	0.2013	0.2308	0.2244	0.2160	0.2482	0.2052	0.1992	0.1524	0.2368	0.8029	0.0391
US-28-NY	0.0173	0.0461	0.0380	0.0300	0.0670	0.0522	0.0446	0.0572	0.0504	0.5239	0.7067
US-31-NY	0.6715	0.6964	0.6707	0.6836	0.7115	0.6803	0.6748	0.6405	0.7013	0.7789	0.3912
US-32-NY	0.7515	0.7744	0.7693	0.7626	0.7882	0.7545	0.7507	0.7152	0.7071	0.4667	0.7839
PAA5	0.6723	0.6977	0.6920	0.6850	0.7129	0.6788	0.6735	0.6370	0.7019	0.4667	0.7071

SAMPLE	US-15-NY	US-22-NY	US-23-NY	US-25-NY	US-28-NY	US-31-NY	US-32-NY	PAA5
US-3-QU	0.0517	0.2946	0.0216	0.2013	0.0173	0.6715	0.7515	0.6723
US-8-QU	0.0231	0.3249	0.0108	0.2308	0.0461	0.6964	0.7744	0.6977
US-18-QU	0.0281	0.3183	0.0094	0.2244	0.0380	0.6707	0.7693	0.6920
US-22-QU	0.0366	0.3098	0.0128	0.2160	0.0300	0.6836	0.7626	0.6850
US-1-ON	0.0180	0.3424	0.0243	0.2482	0.0670	0.7115	0.7882	0.7129
US-3-ON	0.0559	0.3003	0.0206	0.2052	0.0522	0.6803	0.7545	0.6788
US-5-ON	0.0584	0.2937	0.0199	0.1992	0.0446	0.6748	0.7507	0.6735
US-9-ON	0.1029	0.2478	0.0640	0.1524	0.0572	0.6405	0.7152	0.6370
US-11-NY	0.0172	0.0192	0.0114	0.2368	0.0504	0.7013	0.7789	0.7019
US-12-NY	1.0000	0.7549	0.9668	0.8029	0.9561	0.5239	0.3912	0.4667
US-13-NY	0.0141	0.3371	0.0161	0.2429	0.0576	0.7067	0.7839	0.7071
US-15-NY	-----	0.3531	0.0343	0.2910	0.0666	0.7176	0.7960	0.7201
US-22-NY	0.3531	-----	0.3148	0.0897	0.2847	0.4843	0.5637	0.4683
US-23-NY	0.0343	0.3148	-----	0.2210	0.0428	0.6898	0.7675	0.6893
US-25-NY	0.2910	0.0897	0.2210	-----	0.1931	0.5340	0.6102	0.5238
US-28-NY	0.0666	0.2847	0.0428	0.1931	-----	0.6607	0.7440	0.6626
US-31-NY	0.7176	0.4843	0.6898	0.5340	0.6607	-----	0.1500	0.0817
US-32-NY	0.7960	0.5637	0.7675	0.6102	0.7440	0.1500	-----	0.1469
PAA5	0.7201	0.4683	0.6893	0.5238	0.6626	0.0817	0.1469	-----

Note: Strong Dissimilarity => 0.65

Moderate Dissimilarity = 0.65 to 0.45

Weak Dissimilarity = < 0.45

Table 6: Utica Shale magnafacies trace element ratios compared with those from upper continental crust (UCC), and post-Archean Australian Shale composite (PAAS).

Ratio	Immature Québec	Mature Ontario	Post-mature New York	UCC ¹	UCC ²	PAAS ³
Ba/Th	39.54	22.35	55.39	51.40	68.79	44.52
La/Th	3.50	2.80	2.01	2.80	3.30	2.78
Ce/Yb	34.84	17.24	13.79	29.10	30.10	27.10
Ce/Pb	4.07	1.79	1.60	3.20	3.38	4.44
Th/U	2.97	1.68	1.30	3.82	3.91	4.65
U/Pb	0.22	0.20	0.26	0.14	0.13	0.17
Th/Pb	0.59	0.32	0.32	0.54	0.51	0.81
Nb/U	4.09	2.70	2.42	8.93	4.45	4.27
Th/Nb	0.73	0.66	0.67	0.43	0.88	0.77
(Sm/Yb) _N	3.12	1.67	1.91	2.23	2.60	2.14
(La/Yb) _N	12.34	5.32	3.79	9.26	9.75	9.20
(La/Sm) _N	3.95	3.18	1.98	4.16	3.75	4.30
(Lu/La) _N	0.08	0.19	0.27	0.10	0.11	0.11

^N : ratios normalized to chondrite

¹ Upper continental crust; Taylor and McLennan (1985)

² Upper continental crust; Condie (1993)

³ PAAS; Nance and Taylor (1976); Taylor and McLennan (1985); McLennan (1989)

Table 6 shows several key trace element ratios of the analyzed shales compared with upper crustal estimates (UCC) and PAAS. We compare trace element ratios among the three regions and note that there appears to be systematic trace element variability among the three regions. The dissimilarity coefficients presented in Table 5 show that the trace element ratios break into the three regions. There is an overall systematic decrease in Th/Nb, Th/U, Nb/U, Ce/Pb and Th/Pb ratios from the Québec (immature) through the Ontario (mature) to the New York (post-mature) shales (Table 6). Carbonate dilution may cause lower concentrations of La and Th; we believe this is not the case here as we only analyzed those samples that have similar carbonate contents (up to 17 wt. %; Tables 2 and 4). The observed trend towards lower La concentration suggests that the REEs are responding to more than a direct terrigenous particulate source. Similarly, due to the low quartz to clay ratios of all the shales analyzed (0.1 to 0.23), quartz dilution is also negligible. The Th/U and U/Pb ratios (Table 6) are lower and higher, respectively in the post-mature samples than in the immature shales. Systematic variation in U-Th-Pb relationships may represent adsorption of U on organic maceral surfaces at the redox boundary (Ben Othman et al., 1989) causing an increase in U concentration during early diagenesis. As organic matter breaks down during late diagenesis (catagenesis) there will be a preferential increase in U in the surrounding sediments. The relatively low Ba/Th ratios of the Utica Shale magnafacies suggest that the dominant composition of these shales is continental-derived sediments characterized by relatively high Th and low Ba (Vroon et al., 1995). Although we observe slight positive correlations between La and Yb, suggesting the presence of a trace amount of heavy minerals, the REE abundance patterns are uniform (La/Yb)_N < 15 with no evidence of such heavy mineral phases as monazite and allanite based on (Sm/Yb)_N < 2.0 and (La/Yb)_N < 15 (McLennan, 1989).

Most of the shale samples analyzed in our study show low ΣREE values (average: 70 ppm) with a characteristic LREE depletion (ΣLREE average: 57 ppm) relative to the PAAS standard (Table 1). All of the Utica Shale magnafacies samples show low REE values and those from Ontario and New York show depleted LREE (Fig. 4) values as well. The Québec samples show middle REE (MREE) enrichment relative to PAAS. Kidder and Eddy-Dilek (1994) observed this MREE enriched pattern in Pennsylvanian phosphate nodules. Uptake of MREE from enriched pore waters during

early diagenesis could cause this pattern (Awwiller, 1994). Furthermore, the $(La/Sm)_N$ of the shales shows progressive LREE depletion with increasing thermal grade (Table 6).

The Precambrian black shales of the Blondeau Formation of Québec (Tait, 1987), Ordovician Austin Glen Shale of New York (Bock et al., 1994), the Ordovician Valmy and Vanini (Nevada) argillites and the Lachlan (Australia) metashales (Young-Mitchell, 1994, pers.comm.) and the Paleocene-Eocene Wilcox Group shales (Awwiller, 1994) all show low Σ REE values and depleted LREE abundance patterns with respect to PAAS. Awwiller (1994) and others (Tait, 1987; Awwiller and Mack, 1991; Hannigan et al., 1994; Hannigan and Basu, 1995; Hannigan and Basu, 1996) suggest that the observed LREE depletion is due to diagenetic remobilization and relate it to the depth of burial. We analyzed samples with similar mineralogy (low quartz:clay ratios, little to no heavy minerals and low carbonate content; Tables 2-4), organic carbon contents, provenance, depositional environment and early diagenetic histories so that we might assess the evidence for trace element remobilization during late diagenesis, in particular the relationship between clays, organic matter and the lanthanides.

Discussion

Trace Element and REE Variations

There are a number of ways to explain the observed variations in the trace element and REE abundance patterns in shales such as: (1) remobilization during weathering or early diagenesis; (2) sorting of accessory minerals enriched in trace elements and REE; (3) mixing of sediment sources with an LREE-depleted component such as mantle-derived volcanic material (McLennan et al., 1990); and (4) remobilization of trace elements and REE during late diagenesis (Awwiller and Mack, 1991; Awwiller, 1994). Collection of samples for this study involved trenching into outcrops to avoid weathered material. Therefore, we can discount any significant remobilization in these samples due to recent weathering. The utilization of previous geochemical analyses (Hannigan, 1993; Hannigan and Mitchell, 1994) concerning the depositional environment and early diagenetic history of these rocks (carbon-sulfur-iron systematics) allowed us to select similar samples. We submit that early diagenetic mobilization of the trace elements and REEs is not the sole cause of the differences seen in the abundance patterns of these shales. While it is possible that the development of diagenetic phosphates during early diagenesis could account for the MREE enrichment observed in the less mature Québec samples, the same is not true for LREE depletion observed in the more mature Ontario and New York samples. Late diagenetic remineralization of clays and organic matter best explains this depletion. High trace element and REE concentrations characterize the trace element and REE abundance patterns of accessory minerals. It seems unlikely that changes in the relative proportion of heavy minerals such as zircon, sphene, monazite, garnet, and apatite affected the abundances in the Utica Shale magnafacies as we see no evidence in the REE abundance patterns nor any indication of hydraulic sorting. Indeed, fine laminae indicative of distal siliciclastic fill deposited under low energy conditions characterize these shale deposits. Similarly, the HREE abundances of these shales remain flat suggesting no loss of an HREE enriched component. If each of the three regions was sourced by different granitoid plutons, variable amounts of monazite could account for some of the observed LREE depletion, as a result of monazite loss during weathering. In order to identify minerals, we optically examined whole rock polished thin sections and heavy mineral grain mounts of each sample. We found no evidence for heavy mineral sorting in all but the Québec samples which show trace amounts (<0.5 %) of diagenetic apatite. We observe the influence of diagenetic apatite in the REE abundance patterns of samples from Québec (Fig. 4).

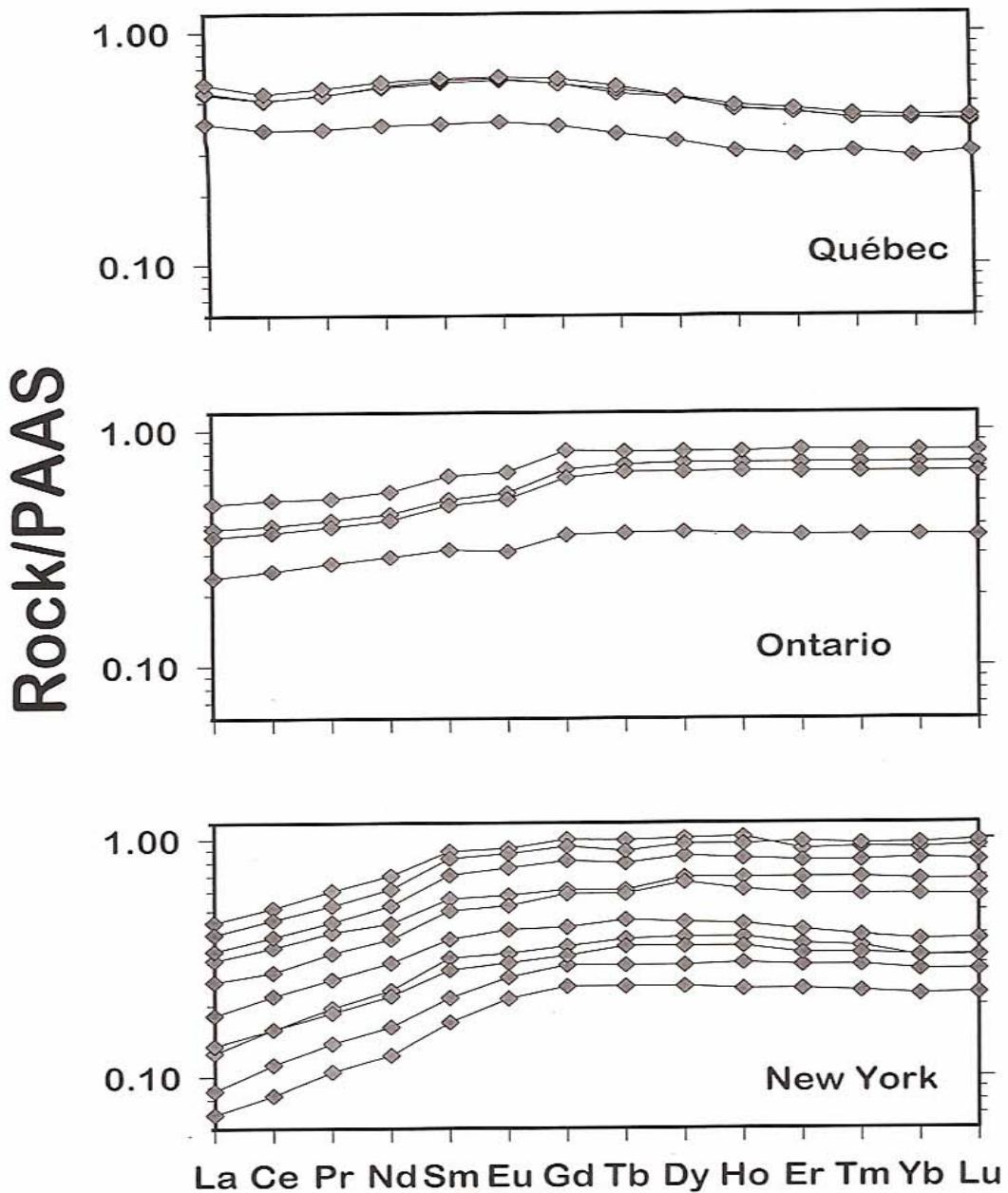


Fig. 4: PAAS-normalized REE abundance patterns of the Utica Shale magnafacies. The samples from Ontario and New York show depleted LREE patterns. Note the middle REE enriched pattern of the Québec samples. This MREE enrichment may be related to the uptake of MREE from enriched pore waters during the early diagenetic formation of authigenic phosphate (Kidder and Eddy-Dilek, 1994; Awwiller, 1994).

Volcanic ash beds do occur throughout the Utica Shale magnafacies of New York (Delano et al., 1990; Goldman et al., 1994). To ensure that the shales analyzed in this study contained minimal volcanic material, we collected shale samples at least 10 meters above or below bentonite layers. There is no evidence for significant background ash input during the deposition of the shales in New York. Also, the deposition post-dates the collision of the arc(s) in the Blountian phase of the Taconic Orogeny (Rast, 1989). While faulting occurred intermittently during the deposition of the lower units of the Utica Shale magnafacies of New York and Québec, there simply is no evidence for an increase in arc-derived sediment input during the deposition of the Utica Shale in these more distal regions of the basin (Baird et al., 1994). The only evidence for any arc-derived sediment comes from the work by Andersen and Samson (1995) which is in no way definitive as the initial ϵ_{Nd} of the Utica shales suggest either juvenile arc material or Grenville material. It is entirely possible

that the Nd-isotopic systematics of the Utica Shale in New York state, as presented by Andersen and Samson (1995) were reset as our results clearly demonstrate REE fractionation subsequent to deposition.

We believe, based on the trace element patterns presented here combined with the work of Andersen and Samson (1995) and Bock et al. (1994), that the dominant siliciclastic source for the three regions was the Grenville basement (or re-cycled sediments originally derived from these granites) with, perhaps a minor, intermittent volcanic component (ash) in the New York samples. Sediment supplied from Grenville basement as the dominant source is more probable than an arc source as these regions are quite distant from the arc. We suggest that the depletion in LREEs observed in the Utica Shale samples from New York and Ontario is due to late diagenetic alteration rather than provenance. Our results show that the LREEs are depleted in the New York samples. Indeed, there is a clear trend to less negative $f_{\text{Sm/Nd}}$ values with increasing thermal grade (Table 1). The $\varepsilon_{\text{Nd}}(0)$ values reported by Anderson and Samson (1995) show a wide range from -16.8 to -12.9. As Bock et al. (1994) showed in a study of the REEs and Nd isotope systematics of the allochthonous correlative to the Utica Shale in New York (Austin Glen Member), fractionation of Sm and Nd occurred at about the time of deposition (470 Ma). Diagenetic remobilization, as described by Milodowski and Zalasiewicz (1991), effected the Sm-Nd system of the Utica Shale magnafacies and therefore the conclusions drawn from the $\varepsilon_{\text{Nd}}(0)$ relationships in these samples are suspect (eg. it is impossible to know whether the trend towards less negative $\varepsilon_{\text{Nd}}(0)$ values up-section in the Utica Shale of New York is attributable to increasing amount of arc-derived material).

Diagenesis and Trace Element Geochemistry of Ordovician Black Shales

The trace element and REE patterns of Ordovician black shales are dissimilar to the PAAS (Figs. 3 and 4). We suggest here that these differences are characteristic of sediments which have undergone extensive late diagenetic alteration and reflect late-diagenetic trace element (and REE) redistribution. Fig. 5 shows the REE abundance patterns of the more mature Ontario and New York samples normalized to an average of the immature Québec samples. There is a significant correlation between thermal maturity and LREE depletion indicative of interstitial diffusion and LREE remobilization at temperatures above 200°C (Dariel, 1978). In particular the LREE, MREE, U, Th and Pb concentrations are statistically different between the three regions with the more mature Ontario and New York being more similar to each other than either location is to the immature Québec samples (average Euclidean dissimilarity coefficient for elements between Québec and Ontario: 0.7925; between Québec and New York: 0.8564; between Ontario and New York: 0.3572). The New York samples show the most pronounced LREE depletion. The post-mature shale samples have relatively high T_{max} values and illitic I/S (Table 3; dry gas) and show the lowest $(\text{La}/\text{Sm})_N$ values (Table 6). Also, Ontario and New York samples demonstrate an increasing U-anomaly with respect to PAAS (Fig. 3). Neither differences in sediment provenance, heavy mineral sorting nor weathering effects can solely account for the heterogeneities in trace element and REE concentrations observed in the shales analyzed in our study. The trace element and REE abundance patterns, as shown in Figs. 3-5, support our assertion that the trace element and REE abundance patterns of Utica shales are not entirely representative of upper crustal abundances but, instead, the abundance patterns of these black shales are the result of significant post-depositional remobilization. Similarly, there are significant correlations between select trace element ratios and extent of diagenesis. Late diagenetic processes such as thermal maturation most strongly affect elements associated with organic matter such as U as well as those elements associated with clays such as the LREEs. Certain trace elements

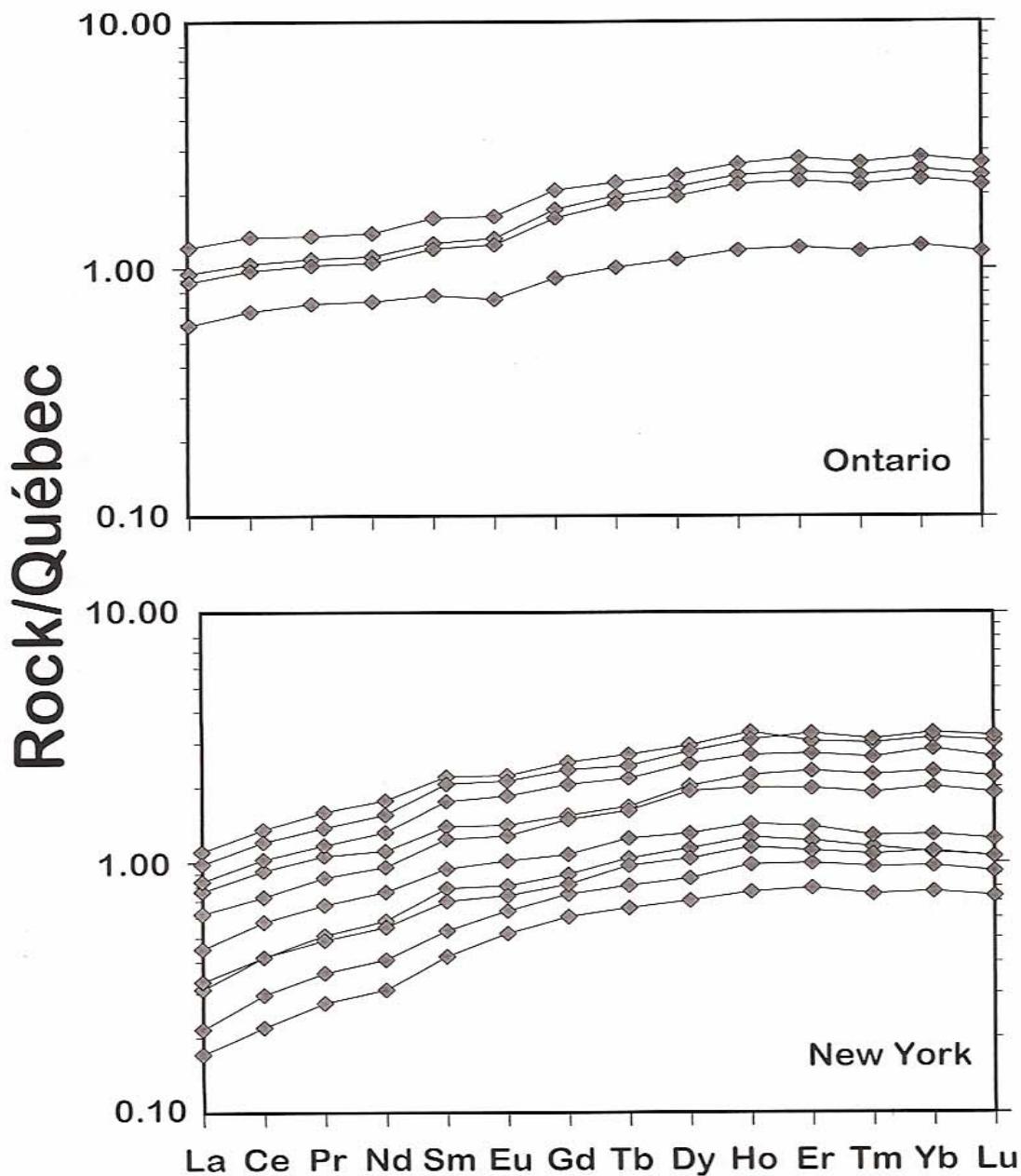


Fig. 5: REE abundance patterns of the New York and Ontario shale samples normalized to an average of the immature Québec samples. The LREE depletion evident in Fig. 4 is shown more clearly when the more mature samples are normalized to the immature samples. Note the overall similarity of the patterns between New York and Ontario. Also note the increasing LREE depletion from Ontario to the more deeply buried New York section.

such as U and the LREEs may remobilize during early diagenesis. Elements most likely to be mobilized are those elements sensitive to redox shuttles as well as those associated with unstable mineral phases such as plagioclase.

Diagenetic Remineralization and REE Geochemistry

Terrigenous input is the primary control on the REE concentration of fine-grained sediments. The primary mechanisms of REE incorporation into sediment are the adsorption from sea water and direct inclusion of terrigenous particulate matter with an inherited REE concentration into the newly deposited sediment (Murray et al., 1991). Detrital clays are the main REE carriers. The overall

Table 7: Rescaled Euclidean dissimilarity coefficient matrix comparing trace element concentration dissimilarity between the three regions studied. Distances Rescaled from 0 to +1.

Element: <i>La</i>	<i>Immature Québec</i>	<i>Mature Ontario</i>	<i>Post- mature New York</i>
<i>Immature Québec</i>	-----	0.7235	0.7625
<i>Mature Ontario</i>	0.7235	-----	0.3235
<i>Post- mature</i>	0.7625	0.3235	-----
<i>New York</i>			

Element: <i>Pr</i>	<i>Immature Québec</i>	<i>Mature Ontario</i>	<i>Post- mature New York</i>
<i>Immature Québec</i>	-----	0.7253	0.7924
<i>Mature Ontario</i>	0.7253	-----	0.3742
<i>Post- mature</i>	0.7924	0.3742	-----
<i>New York</i>			

Element: <i>U</i>	<i>Immature Québec</i>	<i>Mature Ontario</i>	<i>Post- mature New York</i>
<i>Immature Québec</i>	-----	0.7212	0.8652
<i>Mature Ontario</i>	0.7212	-----	0.3875
<i>Post- mature</i>	0.8652	0.3875	-----
<i>New York</i>			

Element: <i>Pb</i>	<i>Immature Québec</i>	<i>Mature Ontario</i>	<i>Post- mature New York</i>
<i>Immature Québec</i>	-----	0.6832	0.7427
<i>Mature Ontario</i>	0.6832	-----	0.2754
<i>Post- mature</i>	0.7427	0.2754	-----
<i>New York</i>			

Element: <i>Ce</i>	<i>Immature Québec</i>	<i>Mature Ontario</i>	<i>Post- mature New York</i>
<i>Immature Québec</i>	-----	0.7924	0.7387
<i>Mature Ontario</i>	0.7924	-----	0.3412
<i>Post- mature</i>	0.7387	0.3412	-----
<i>New York</i>			

Element: <i>Nd</i>	<i>Immature Québec</i>	<i>Mature Ontario</i>	<i>Post- mature New York</i>
<i>Immature Québec</i>	-----	0.7864	0.7465
<i>Mature Ontario</i>	0.7864	-----	0.3423
<i>Post- mature</i>	0.7465	0.3423	-----
<i>New York</i>			

Element: <i>Th</i>	<i>Immature Québec</i>	<i>Mature Ontario</i>	<i>Post- mature New York</i>
<i>Immature Québec</i>	-----	0.7458	0.7754
<i>Mature Ontario</i>	0.7458	-----	0.3414
<i>Post- mature</i>	0.7754	0.3414	-----
<i>New York</i>			

Note: Strong Dissimilarity = > 0.65
 Moderate Dissimilarity = 0.65 to 0.45
 Weak Dissimilarity = < 0.45

burial rate, which controls the sediment's exposure time to seawater may cause the low ΣREE of these fine-grained sediments. As the conditions approach the "oil window" (principal zone of oil generation ~50°–150° C), K-feldspar and plagioclase either dissolve or albitize. More significant than feldspar dissolution in shales is the transformation of detrital smectitic I/S to illitic I/S as well as the development of small amounts of authigenic chlorite at greater burial depths. We observe this transformation in our shales (Table 3). During burial diagenesis, the shales behave as open chemical

systems (Awwiller, 1994). The three regions of Utica Shale have undergone variable amounts of burial diagenesis (Bertrand et al., 1983; Wallace and Roen, 1989; Barker et al., 1990). Dissolution of the detrital minerals occurs during diagenesis. Zircon, apatite and iron-titanium oxide are the only common heavy minerals that might survive in the more deeply buried rocks such as those from New York State. We see no evidence for zircon, iron-titanium oxides or apatite in the New York samples. The more shallow buried samples from Québec show no evidence of heavy minerals such as garnet and monazite; however, a minute amount of iron-titanium oxide and diagenetic apatite may persist as these samples are not re-magnetized (Cottrell, 1996, pers.comm.).

XRD analyses of oriented clay-size fraction samples, from the current study (Table 3) as well as others, shows an increase in illitic I/S as well as authigenic chlorite from Québec to New York (Bertrand et al., 1983; Macauley et al., 1983; Turner, 1985). Studies, similar to our current study, of mudrocks which have undergone extensive burial diagenesis suggest that preferential sequestration of the LREEs relative to the MREEs in authigenic illite/smectite (I/S), produces a diagenetic fluid enriched in MREE (Mack and Awwiller, 1990; Awwiller and Mack, 1991). Shannon (1976) demonstrated that, due to the size of the CN-12 ionic radii of the trivalent LREE, they may commonly substitute, in low concentrations, for potassium in illite (in the I/S interlayer site). The diagenetic products of the Wilcox Group shales (Awwiller and Mack, 1991) record mineralogic fractionation of Sm from Nd by smectite illitization. These authors suggest that the REEs must be migrating from shales into the pore waters during or subsequent to illitization.

Another important aspect of the effect of late diagenetic processes on trace elements, particularly the lanthanides, is the role of organic matter. As electrons are removed to form trivalent lanthanide ions (Ln^{3+}), they are taken preferentially from the 6 s and 5 d orbitals. For lanthanides, the regions of greatest 4 f electron density simply do not extend far enough out from the nucleus for these electrons to take part, to any great extent, in bonding (Cotton, 1991). It is due to these special chemical properties of the lanthanides that they are valuable and unique to the study of geologic processes such as diagenesis. Known organolanthanide reactions include insertion reactions of carbon monoxide and C-O bond breakage (Imamoto et al., 1984). Lanthanides also complex with organic ligands such as porphyrins, tetrapyrroles, and cyclopentadienyls (Wong et al., 1974; Fenton et al., 1981; Mohamed et al., 1990; Manning et al., 1991). These compounds are found in both sediments and crude oils (Manning et al., 1991; Stille et al., 1993; Litchfouse et al., 1994). The lanthanide concentration in unaltered biologically derived organic products is low (average: 45-100 ppb; Schaverien, 1994). This low concentration can be attributed to the fact that there is no known role for lanthanides in biological reactions, although they are known to substitute isomorphously for calcium ions in some metalloproteins (parvalbumin, thermolysin; Cotton, 1991). The lanthanides are also known to substitute for calcium in certain calcium-based systems in the absence of calcium (Falke et al., 1981). However, the total REE concentrations observed in sedimentary organic matter and crude oils shows a broader range from 10 ppb in crude oils to 15,000 ppm in kerogens and bitumens (Tait, 1987; Manning et al., 1991; Bros et al., 1992; Mossman et al., 1993). Clearly, this higher bulk REE concentration in the organic matter of shales is not due to the presence of biologically derived unaltered, primary organolanthanide complexes. It is possible that the organic matter of shales acquires lanthanides both within the water column and within the sediment during early diagenesis, as discussed below.

In order to assess the role of organic matter in the preservation of lanthanides, a mechanism by which organic matter acquires lanthanides during the deposition and diagenesis of shales must be established. While much work needs to be done before mechanisms and their impact on REE distribution/partitioning can be understood, it is possible to surmise a mechanism for REE incorporation into sedimentary organic matter and REE remobilization into the solid organic fraction during diagenesis by utilizing what is known about organolanthanide chemistry. Lanthanides often reside in the lattice-sites of the silicate minerals of sedimentary rocks. Exchangeable REEs residing

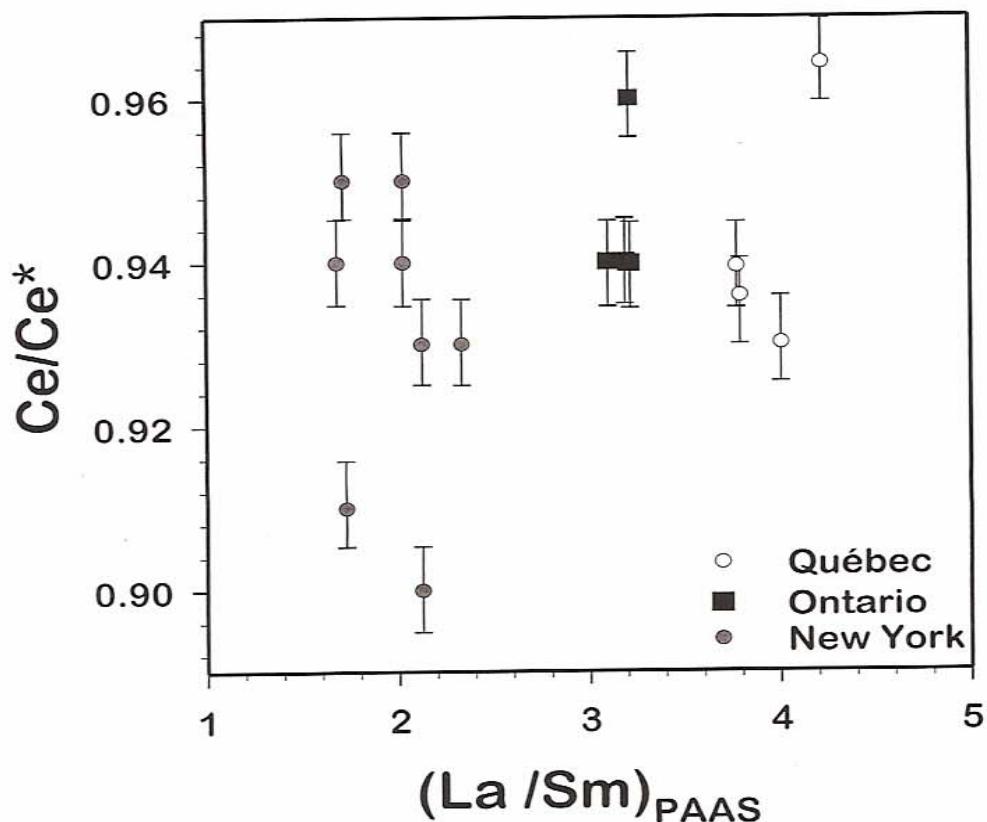


Fig. 6: Ce/Ce* versus (La/Sm)_{PAAS} plot demonstrating LREE fractionation in the thermally mature Utica Shale magnafacies samples. We calculated the uncertainty associated with the Ce/Ce* measurement and calculation by calculating the Ce/Ce* of each replicate and then taking the average and standard deviation of that data set. We did not propagate the uncertainties of La, Ce and Pr through the Ce/Ce* calculation in order to avoid an artificially high error. Several samples show slight Ce anomalies. As Ce is an LREE we explored the possibility that the Ce anomaly might be an artifact of diagenesis as suggested by Murray et al. (1991). The proportional decrease of both Ce/Ce* and (La/Sm)_{PAAS} with increasing diagenetic alteration supports our contention that the LREEs are preferentially remobilized during late diagenesis and leads to the conclusion that the Ce anomaly may be the result of redox and/or diagenesis.

in soluble non-silicate phases such as calcite and apatite and on clay-specific sites (exchangeable interlayer sites and basal surfaces; Ohr et al., 1991) enter a marine depositional system either through rivers or as aerosols. Lanthanides not removed from the dissolved load of rivers in estuaries (areas enriched in REE; Goldstein and Jacobsen, 1988; Andersson et al., 1994) or bound into insoluble phases within the marine water column may adsorb onto mineral and organic maceral surfaces. The lanthanides will exchange freely between both organic substances and mineral surfaces. In order to be complexed by an organic ligand, lanthanides must react with polar or non-polar X-H bonds via a concerted σ -bond (C-C bond) metathesis mechanism thereby chelating with ligands that are part of polar associations of organic molecules. Lanthanides behave in this way because the valence state difference is one rather than the necessary two. Thermodynamic stability, with one preferred oxidation state, cannot be achieved through redox shuttles such as oxidation addition or reductive elimination. The most likely complexing mechanism is activated interstitial diffusion (Dariel, 1978). Activated interstitial diffusion requires that rare earth elements collapse due to 4f-5d electron promotion and consequently a collapse of the atom to a smaller size. Once this collapse occurs, the lanthanide is released from its site and is free to be bound by organic ligands. It should be noted that LREE are the most susceptible to this diffusion mechanism which can occur at temperatures in excess of 200°C (beyond the oil window). Stabilization of lanthanides can occur prior to deposition

and also during early diagenesis. Uncomplexed lanthanides are transported down column as part of the dissolved inorganic fraction (DIC) and reach the sediment-water interface still adsorbed onto exchangeable sites as described above. During early diagenesis, lanthanides are desorbed from these sites and may be stabilized by the highly reactive organic ligands or complexed by diagenetic clays. Mohamed and others (1990), suggested that the chelated hydrogen of the organic ligand is replaced by the lanthanides. They also remarked that the hydrogen of the hydroxyl groups common to organic macromolecules is involved in the chelation due to its low pK value (3.75). Once the lanthanide is stabilized in this manner, diffusion ceases. The stabilized MREE and HREE are not affected by catagenesis as the organic ligand is a short chain π -adducted organic molecule insensitive to organic matter breakdown during late diagenesis. It should be noted, however, that π -bonded LREE are still susceptible to bond breakage and diffusion due to their vulnerability to atom collapse. At present, our understanding of how REEs are “re-partitioned” during diagenesis is limited. The REEs appear to re-incorporate into long-chain/heavy organic compounds (kerogen, bitumen) during diagenesis. A small portion may be incorporated into lighter/liquid hydrocarbons but, from a mass balance perspective, expulsion of crude oil cannot account for the LREE depletion (assuming originally flat patterns relative to PAAS) observed in the New York and Ontario samples.

As Ce is an LREE and we have demonstrated that the LREEs are remobilized during burial diagenesis, it is possible that the small negative Ce-anomalies detected in the Utica Shale magnafacies samples are simply an artifact. The significance of the Ce anomaly in deciphering the redox conditions of depositional environments hinges on the assumption that Ce is not significantly remobilized during diagenesis. Murray et al. (1991), noting a progressive diagenetic LREE fractionation in deep sea sediments from the Japan Sea, suggested that the magnitude of Ce/Ce* is a passive response to the diagenetic transfer of trivalent LREE from the sediments to the interstitial water. Fig. 6 shows the relationship between the Ce-anomaly and LREE depletion. There is an overall decrease in Ce/Ce* with decreasing $(La/Sm)_{PAAS}$ further supporting our assertion that the LREEs are preferentially remobilized during late diagenesis. It appears, based on our results, that the Ce anomaly, if present at all, may be the result of competing processes including redox and late diagenetic remobilization.

Conclusions

The trace element and REE abundances of the Utica Shale magnafacies samples analyzed in this study, support the contention that the dominant siliciclastic source for the Taconic Foreland basin shales was Grenville basement (or sediment originally derived from Grenville basement). The strong influence of a continental crust source is seen in the strong Nb-Ta anomalies of the Ontario and New York samples. Burial diagenesis can affect the Nd isotope system. As the LREEs are depleted in the more deeply buried New York samples, so the $f_{Sm/Nd}$ is less negative. This supports our contention that the conclusions drawn from Sm-Nd isotope systematics are in question as the effect of diagenesis on the $^{147}Sm/^{144}Nd$ ratio will strongly affect the $\epsilon_{Nd}(0)$ of the samples studied and may induce a bias towards more negative values. There are progressive changes in trace element ratios such as Th/U and U/Pb with increasing extent of diagenesis. These progressive changes hint at the role of organic matter in the preservation of trace element abundances, particularly in rocks which have undergone extensive burial diagenesis. The REE abundance patterns do not support the notion that the Utica Shale magnafacies contains a significant amount of arc-derived material. There are three types of REE patterns in the Utica Shale magnafacies. LREE depleted patterns are common for the more deeply buried (thermally mature) samples. The shallow buried Québec samples show MREE enrichment related to the higher concentration of phosphate. The LREE depletion observed in the shales that have undergone extensive burial diagenesis (Ontario and New York) supports the contention that the shales behaved as an open system for the more mobile trace elements such

as the LREEs. None of the samples showed effects of heavy mineral sorting or carbonate-quartz dissolution. We conclude that remobilization of REEs occurs during late diagenesis, causing LREE loss from the mudrocks during illitization and/or organic matter breakdown during catagenesis. The results of this study clearly suggest that the role of organic matter in the preservation of trace element abundances may be significant.

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