Effect of diagenesis on trace element partitioning in shales

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Abstract

In order to investigate the partitioning of trace elements in mineral phases of black shales and diagenetic remobilization of trace elements within these phases, we isolated major black shale components (sulfide, carbonate, silicate and organic) and analyzed the isolated fractions as well as corresponding whole rock for their trace element composition by DRC ICP-MS. This study focused on black shales of different grades of thermal maturity from the Ordovician Utica Shale Magnafacies of Quebec (USM) (immature: T_{max} 20–50 °C, $R_o < 0.5$), Ontario (mature: T_{max} 50–140 °C, R_o 0.5–0.8), and New York (post mature: $T_{max} > 140$ °C, $R_o > 1$). Analysis of the isolated rock fractions revealed that the carbonate fraction preserves a sea water-like rare earth elements (REE) abundance pattern with enrichment of the heavy rare earth elements (HREE–Dy–Lu) relative to light rare earth (LREE–La–Sm). The sulfide and organic fractions show a slight enrichment in the LREE. Mass balance calculations showed that the organic fraction contains up to about 20% of total trace element content of the whole rock with the sulfide and carbonate fractions each containing less than 10%. The partitioning and fractionation of trace elements between different phases may have important implications for paleoenvironmental reconstructions and provenance studies. Our data suggest that the whole rock signature may be less representative of source area or depositional environment but rather reflects the diagenetic history. This is especially the case in organic rich sediments such as black shales where the organic fraction hosts up to 20% of the trace element content of the whole rock.
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1. Introduction

Assessing the source of sediments in both marine and terrestrial basins is traditionally accomplished through the use of trace element geochemistry. Specifically, these provenance studies utilize the relative abundances of trace elements and rare earth elements (REE) to define parent material. The use of trace elements in provenance studies is based on the premise that post-depositional processes such as surficial chemical and mechanical weathering, re-working, re-suspension, and re-deposition do not significantly alter the chemistry of certain trace elements. Most important to the application of geochemical techniques to sedimentary rock provenance is the assumption that trace elements, more specifically the REE (La to Lu) are neither lost nor gained during the processes of rock formation (diagenesis). Several studies (Hellman et al., 1979; Duddy, 1980; Sholkovitz, 1990; Milodowski and Zalaskiewicz, 1991; Ohr et al., 1994; Lev et al., 1999; Lev and Filer,

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2004a,b) have demonstrated that diagenesis can significantly mobilize or fractionate REE in sediments leading to disparities between the rock signature and presumed parent material. In addition, it is often assumed that, if the relative abundances of these elements are altered by diagenetic processes, the alteration occurs in a predictable manner; a manner that is explicit to the geochemist. For example Lev et al. (1999) suggested that early diagenesis of organic rich sediments and formation of diagenetic apatite can affect the chemistry of these sediments leading to redistribution of the REE between different shale components, but the overall rock chemistry remains the same since this change only occurs on a mineral scale (no mass transfer involved). Their assumption is based on the fact the clay-sized material are relatively impermeable and hence do not allow complete loss of the REE. However, Milodowski and Zalaskiewicz (1991) and Awwiller (1993) showed that during burial diagenesis, mudrocks act as open systems allowing for exchange of material between adjacent sediment units leading to significant fractionation and/or loss of REE. Bloch and Hutcheon (1992) have also proposed open system diagenesis in shales.

Because provenance studies often rely on radiogenic isotope data to define the parent material, fractionation of trace elements can have a profound impact on the conclusions drawn not only about the parent material but consequently about the paleoenvironment. For example, if the REE are fractionated during diagenesis leading to a preferential loss of the light REE (La–Sm) relative to the original abundance of these elements in the parent rock, this can significantly alter the Sm–Nd isotopic signature (McLennan, 1989; Bock et al., 1994, 2004; Hannigan and Basu, 1998; Hannigan et al., 2004). Also the loss of organic matter during thermal maturation of black shales and associated remobilization of trace elements may impart a diagenetic signature in black shales which is different from depositional signature (Raiswell and Berner, 1987). Maturation of organic matter may lead to the production of aggressive pore fluids (organic acids) capable of altering the whole rock chemistry (Kawamura and Kaplan, 1987). This alteration may have profound effects on the rock signature when reconstructing paleodepositional environments (Mack and Awwiller, 1990; Awwiller and Mack, 1991, McDaniel et al., 1994; Andersen and Samson, 1995). Lev et al. (1999) reported that, as a consequence of diagenetic reactions, REE are redistributed on a mineralogic scale and that the REE, as well as uranium, and their associated isotopic systems (Sm–Nd and U–Pb) can

reflect a diagenetic overprint rather than the source area and depositional conditions. Conversely, other studies have revealed that processes of sedimentation and diagenesis do not significantly fractionate these elements, and as a result the Sm–Nd isotope system can be used to both age date and to reconstruct palaoeenvironmental conditions (Chaudhuri and Cullers, 1979; Stille and Clauer, 1986; Ugidos et al., 1997; Andersson et al., 2003).

In order to assess the effect of diagenesis on trace element partitioning, we employed sequential leaching to isolate major components of black shale (siliciclastic, organic, carbonate, and sulfide) and analyzed these components for their trace element composition. It is important to note that in these rocks the dominant mineral phase is siliciclastic but in this research we computed the elemental composition associated with this phase as the difference between the whole rock and sulfide, organic and carbonate phases. The mineralogy of our study unit, the Ordovician Utica Shale Magnafacies (USM) is more complex than just the silicate, organic, carbonate, and sulfide fractions. Although the dominant fraction is siliciclastic, fractionation and remobilization of trace elements from other phases more susceptible to diagenetic alteration may alter the whole rock trace element chemistry. We therefore focused our attention on the susceptible phases such as organic, sulfide, and carbonate. Another diagenetic phase (phosphate) that can affect the trace element chemistry in black shale sufficient to alter provenance information, is not accounted for in this study. Kidder et al. (2003) reported that a significant effect on the trace element chemistry of black shales by diagenetic phosphate only occurs when the content of P_2O_5 in these rocks is greater than 5.0 wt.%. Their data suggests that in black shales where the P_2O_5 content is less than 0.5 wt.% typical La–Th–Sc distribution is common. A majority of the samples analyzed in this study have P_2O_5 content less 0.5 wt.%. The effect of diagenetic apatite on the REE chemistry of black shales remains unclear when the content of P_2O_5 is between 0.5 and 5.0 wt.% (Kidder et al., 2003). Following our leaching procedure, it is likely that the phosphate fraction was leached partly alongside the carbonate fraction or with the silicate fraction.

The rationale for the approach adopted in this study, (isolation of different shale components) is to better understand the effects of organic matter diagenesis (thermal maturation) on the redistribution of the REE and other trace elements in black shales. Since most studies on the effects of diagenesis on trace element

composition in organic rich sediments have looked at whole rock composition, it remains unclear which rock component dominates the trace element chemistry of black shales and how maturation of organic matter and production of aggressive pore fluids may alter the chemistry of these rocks.

2. Geologic setting

To adequately assess the effect of diagenesis on trace element composition, a unique suite of rocks is required. The units must be well constrained in time and must have undergone variable degrees of diagenesis. In addition, the units chosen must share a common provenance. The Utica Shale Magnafacies (USM; Fig. 1) of Quebec (immature: T_{max} 20–50 °C, $R_o < 0.5\%$), Ontario (mature: T_{max} 50–140 °C, R_o 0.5–1.0%), and New York (post mature: $T_{max} > 140$ °C, $R_o > 1.0\%$; Hannigan and Basu, 1998) provides the ideal suite of rocks to explore the hypothesis that organic matter maturation (re: diagenesis) leads to significant fractionation of trace elements in black shales. The T_{max} is based on graptolite reflectance (Betrand, 1987; Hannigan, 1997).

The USM was deposited in the Taconic Foreland Basin approximately 420 Ma during the Taconian Orogeny (Bradley and Kidd, 1991). At this time the Taconic Terrane (a volcanic island arc) collided with the passive margin of Laurentia resulting in an increase in water levels that saw a break in the deposition of carbonate material. Carbonate sedimentation on the passive continental margin then gave way to flysch deposits. Flysch deposits became common together with the early deposition of siliciclastic sediments from weathering of the upheaved masses. Stratigraphic studies indicate that in New York, the USM sits conformably on the Trenton limestone and in some cases the two facies have been found to overlap (Brett and Baird, 2002). The organic matter in the USM is entirely marine in origin since these sediments were deposited in the Middle to Late Ordovician period before the proliferation of terrestrial vascular plants. The USM has been constrained in time by graptolite biostratigraphy and bentonite chronostratigraphy (Samson et al., 1995; Goldman et al., 1994; Mitchell et al., 1994, Gordon and Brett, 2002). The Blue Mountain and Collingwood formations from Ontario and the Lotbiniere formation from Quebec are the stratigraphic
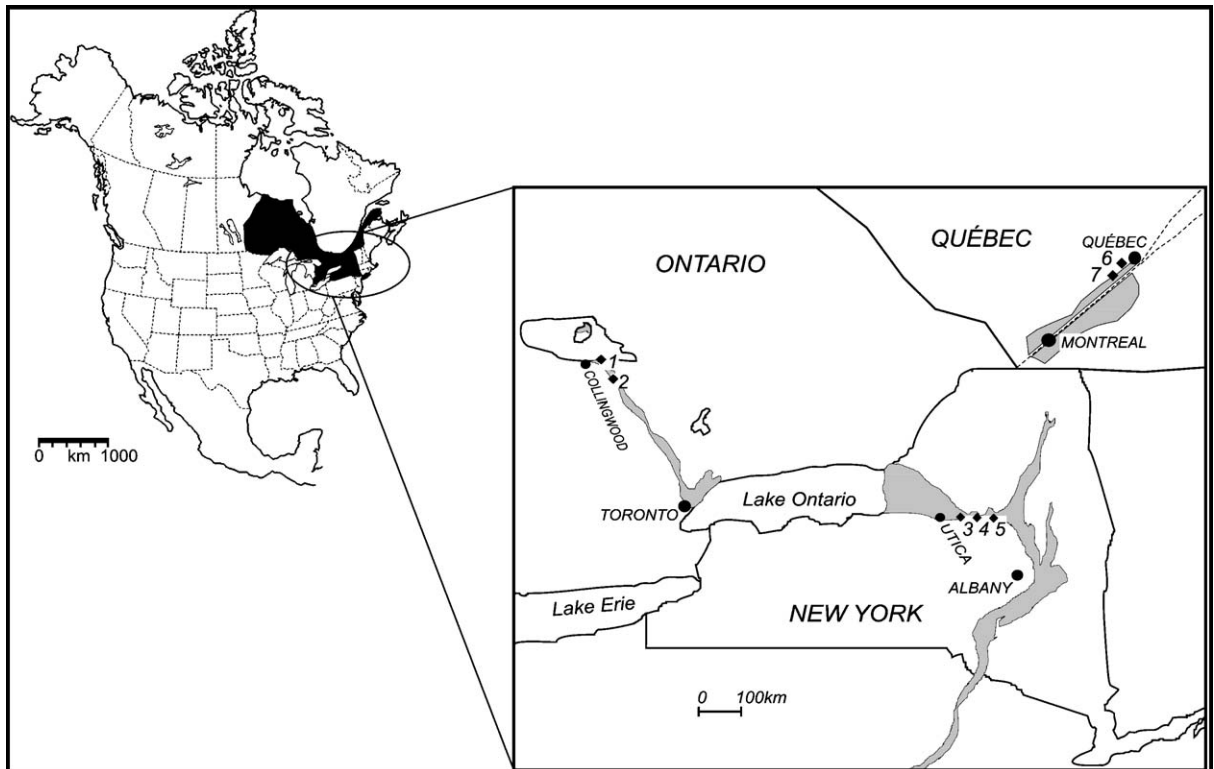

Fig. 1. Location of sample sites for the Utica shales magnafacies of Quebec, Ontario and New York (modified from Hannigan and Basu, 1998). Sample collection sites include: Quebec, 6 and 7; Ontario, 1 and 2; and New York, 3, 4 and 5.

Table 1
Depth, stratigraphic intervals and graptolite zones of samples analyzed in this study

Samples	Depth [a]	Stratigraphic interval	Graptolite zone
Quebec (immature)			
USM 32	32	Lotbiniere	C. *Spiniferous*
USM 44	44	Lotbiniere	C. *Spiniferous*
QB 23073	73	Lotbiniere	C. *Spiniferous*
QA 23110	110	Lotbiniere	C. *Spiniferous*
QE 23109	109	Lotbiniere	C. *Spiniferous*
QK 23411	411	Lotbiniere	C. *Spiniferous*
Ontario (mature)			
OGS-104	104	Blue mountain	G. *Pygmaeus*
OGS-06	106.2	Collingwood	G. *Pygmaeus*
OGS-111	111.3	Collingwood	G. *Pygmaeus*
OGS-753	228.2	Collingwood	G. *Pygmaeus*
OGS-762.5	231.1	Collingwood	G. *Pygmaeus*
New York (post mature)			
FAA	XA	Flat creek	G. *Pygmaeus*
CURA	XA	Flat creek	G. *Pygmaeus*

[a] Depth in metres from base of core, XA = unavailable.

equivalents of the USM of New York. Shale samples used in this study (Table 1) include drill core and trenched outcrop samples, which are spatially time correlative. Samples were carefully selected to avoid bentonite beds that are very common in this basin (Goldman et al., 1994).

3. Methods

Fig. 2 is a schematic presentation of the experimental procedure used in this study. Sequential extraction methods for isolating different rock fractions have been used by various authors, (Tait, 1987; Ohr et al., 1994; Tessier et al., 1979; Dubinin and Strekopytov, 2001; Bayon et al., 2002). Our work built on the extraction technique of Tait (1987). The technique involves the use of various acids with the application of heat to isolate different shale fractions. The treatment of sediments with various acid and bases has been widely used in the study of leachable mineral fractions. In most of these studies, dilute HCl or acetic acid has been used to obtain the carbonate fraction (Sondag, 1981); concentrated HF and a combination of concentrated HF and $HClO_4$ for silicate digestion (Tessier et al., 1979; Bayon et al., 2002); concentrated HNO_3 and aqua regia for sulfide extraction (Chao and Theobald, 1976); H_2O_2 for organic matter removal (Bayon et al., 2002).

The amount of reagent used and amount of sample treated varied depending on sample availability and the amount of extract needed for analysis. In most

sequential extractions the more easily leachable fractions are extracted first followed by the more refractory fractions. The redistribution of elements between different mineral phases during sequential extractions and the problems associated with this technique have been investigated by a number of authors (Whalley and Grant, 1994; Rapin et al., 1986; Kheboian and Bauer, 1987; Martin et al., 1987). It is believed that the dissolution of sedimentary mineral phases results in the release of elements associated with that phase.

3.1. Sequential leaching (isolation of shale fractions)

3.1.1. Isolation of carbonate fraction

We used about 25 g of finely powdered rock sample (<60 mesh) to which we added, in a 250 ml Teflon beaker, 50 ml of trace metal grade acetic acid. The mixture was placed on a hot plate set at 60 °C in a fume hood. The mixture was stirred from time to time until the reaction ceased (up to about 12 h). When a sample stopped fizzing, it was taken off the hot plate and allowed to cool. The supernatant solution was carefully siphoned off avoiding any agitation. This supernatant is here operationally defined as the carbonate fraction. This fraction was dried slowly and digested using ultra pure HNO_3 before subjecting it to trace element analysis by dynamic reaction cell inductively coupled mass spectrometry (DRC ICP-MS).

3.1.2. Isolation of silicate fraction

The residue from carbonate extraction was washed several times using Milli Q water (18.3 MΩ) and dried in the oven at 60 °C. Ultra pure hydrofluoric acid (HF) was added in 10 ml increments to this fraction. The reaction can be explosive so HF was added slowly to avoid violent explosion and subsequent loss of sample. A Teflon watch glass was placed on top of the beakers allowing the
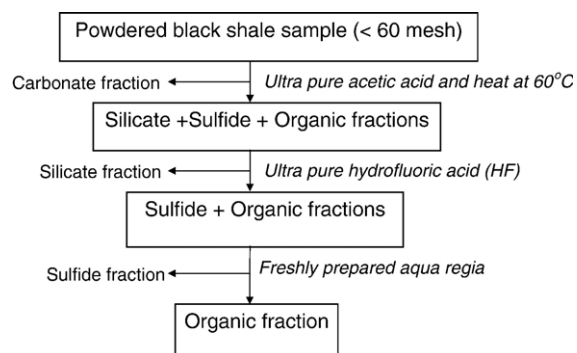

Fig. 2. Tree diagram showing sequential leaching technique and separation of shale components.

samples to breathe to prevent gas build up (SiF_4). The sample was stirred at 12-h intervals during the entire reaction period. The bottles containing the samples were balanced in pairs and centrifuged at 3500 rpm for 20 min. The supernatant liquid containing the silicate fraction was decanted after centrifuging. The whole silicate extraction procedure takes about 96 h to allow complete HF reaction with samples. After acid decantation, distilled water was added to the bottles and they were placed on a reciprocating shaker for 30 min. The bottles were centrifuged again at 3500 rpm for 20 min. The residue contains the sulfide-organic matter fraction.

3.1.3. Isolation of the sulfide fraction

The residue from the silicate fraction extraction containing the sulfide and organic matter fraction was subjected to further treatment to isolate the sulfide fraction. The residue was transferred into 250 ml Teflon bottles and each bottle was covered with filter paper to allow evaporation of water. The bottles were placed in a fan-forced oven at 50 °C and allowed to dry. After drying, 25 ml of freshly prepared aqua regia solution was added and the bottles were placed in a hot water bath containing preheated water. The mixture was simmered for three hours at about 90 °C. Syringe filters (0.45 µm) were used to extract the aqua-regia solution that contains the sulfide fraction. It is possible that treatment of this residue using aqua regia may partially oxidize the organic matter in our samples thus enriching the sulfide fraction with part of the organic fraction. Since we did not analyze the residue before and after treatment with aqua regia it is difficult make any conclusions about the degree of organic matter alteration by this mixture of acids. So for the purpose of this work the obtained fraction is operationally defined as the sulfide fraction. This fraction was diluted before subjecting to trace element analyses by DRC-ICP-MS. The filters were returned into a 250 ml Teflon beaker to which Milli Q water was added. We balanced the beakers in pairs and agitated very gently to keep filters intact. The solution was centrifuged (10 000 rpm) for 10 min. Samples are washed using MQ water until a neutral pH (~7.0) was obtained. The remaining sample was dried in a fan forced oven set at 50 °C. The heated material was allowed to cool and was digested at 90 °C using ultra pure HNO_3. After cooling, a few drops of metal grade H_2O_2 was added to ensure complete digestion of organic matter.

3.2. Analytical methods

Trace element content of isolated fractions and of corresponding whole rock was measured by Dynamic Reaction Cell Inductively Coupled Plasma mass Spectrometry (DRC-ICP-MS, Perkin Elmer Sciex). Standards containing the rare earth elements and trace elements were prepared in a linear range from 1 ng/g to 1000 µg/g. Internal standard containing 40 µg/g Indium ([115]In) was added to each blank, standard and sample. The internal standard was used to correct for instrumental drift. SDO-1 (USGS Ohio Devonian shale) was measured as an unknown to monitor external precision. Trace element concentrations were within 5% of the reported values of this matrix standard. Relative standard deviations for sample concentrations are better than 5% for all analytes.

Total carbon, organic carbon, total sulfur analyses were conducted at the SGS analytical laboratories in Canada using the total carbon and sulfur Leco analyzer with detection limits of 0.01% (Method CHM118 and CHM119). Total inorganic (mineral carbon) was calculated as the difference between total carbon and organic carbon. Major element (P_2O_5) analysis was carried out by XRF with detection limits of 0.1% at the SGS-XRAL analytical laboratory.

4. Results

4.1. Total carbon, organic carbon, and total sulfur

Total carbon, total organic carbon, inorganic carbon and total sulfur concentrations of whole rock are given in Table 2. Total carbon content range from 1.2 to

Table 2
Total carbon, organic carbon, inorganic carbon and total sulfur, content (wt.%) in selected whole rock samples of the Utica shales of Quebec, Ontario and New York (New York)

Sample identity	C_T	S_T	C_{org}	C_{inorg}
Quebec (immature)				
QA 23110	1.23	0.59	0.36	0.87
QB 23073	1.66	0.37	0.19	1.47
QK 23411	4.35	0.98	0.94	3.41
QE 23109	9.38	1.24	5.16	4.22
Ontario (mature)				
OGS 104	2.18	1.84	1.53	0.65
OGS 106	8.33	1.17	2.92	5.41
OGS 111	13.10	0.59	3.77	9.33
OGS 753	7.66	0.21	0.49	7.17
OGS 762.5	10.50	0.17	0.12	10.38
New York (post mature)				
FAA	10.10	0.29	0.75	9.35
CPHC	4.35	0.45	0.99	3.36
CURA	6.80	0.50	1.71	5.09

C_T=total carbon, S_T=total sulfur, C_{org}=organic carbon and C_{inorg}= inorganic carbon.

13.14 wt.%. The average total carbon content of the Ontario samples was higher than that in the New York and Quebec samples. Total sulfur content range from 0.17 to 1.84 wt.%. The lowest S content measured (0.17 wt.%) and the highest S content (1.84 wt.%) all belong to mature samples from Ontario. Total organic carbon content range from 0.12 to 5.16 wt.% that is consistent with values reported by Hannigan and Basu (1998) for these rocks. We calculated the amount of inorganic carbon as the difference between total carbon and total organic carbon. Inorganic carbon in all samples range from 0.65 to 10.38 wt.% with the Ontario and New York samples having a slightly higher inorganic carbon content compared to the Quebec samples. The concentration of P_2O_5 in the whole rock samples range between 0.011 and 0.50 wt.% with slightly higher P_2O_5 content in the mature and post mature samples when compared to the immature samples.

4.2. Rare earth elements in whole rock and corresponding fractions (carbonate organic and sulfide)

Rare earth element data for whole rock and corresponding rock fractions (carbonate, organic and sulfide) are presented in Table 3. Rare earth element abundance patterns of whole rock, normalized to the North American Shale Composite (NASC), (Gromet et al., 1984) are shown in Fig. 3. The REE in the whole rock samples are similar to NASC both in absolute REE content and relative abundances. The sum of rare earth elements (ΣREE) in the whole rock samples ranges between 50 and 297 ppm. Similar to results obtained by Hannigan and Basu (1998), lower REE contents are associated with the post mature samples while higher REE contents are associated with the immature samples. When compared to chondrite normalized patterns the NASC normalized REE patterns show a slight enrichment of the light and middle rare earth elements (La–Dy), and a slight depletion of HREE (Ho–Yb). Chondrite normalized patterns show a higher enrichment of the LREE, a slight depletion of Eu relative to neighboring REE and flat HREE. Relative to chondrite, the contents of LREE in NASC is about 100 times higher and the content of the HREE is about 10 times higher which may account for observed differences in REE patterns with different normalization values.

The carbonate fraction is enriched in the HREE relative to the LREE (($La/Yb)_N$ < 1) (Fig. 4). The degree of enrichment is variable with no definite trend of higher enrichment in one group of samples when compared to the others. The sulfide fraction shows a slight enrichment in the content of LREE relative to HREE (Fig. 4). There is an enrichment of the redox sensitive rare earth element (Eu) relative to the neighboring REE in this fraction. This enrichment may be a characteristic inherited from the parent material. We also observe a slight positive cerium anomaly (Ce/Ce* > 1) associated with a majority of the sulfide fraction. The Ce/Ce* anomaly tends to be higher in the immature samples relative to the mature and post mature samples (average Ce/Ce* = 1.1 immature, 0.93 in mature and 0.89 in post mature samples). The sum of LREE (La–Sm) on the average is higher in the immature samples when compared to the mature and post mature samples. There is a slight enrichment of the LREE relative to the HREE in the organic fraction. The positive Ce/Ce* anomaly observed in the sulfide fraction does not appear in the organic fraction. There is much variability in the absolute concentration of REE in the organic fraction (Fig. 4) when compared to the other shale fractions and the corresponding whole rock. Relatively higher ΣREE are found in the organic fractions in the post mature samples.

4.3. Other trace elements in whole rock and corresponding rock fractions

Elemental concentrations of Ba, Th, U, Sr, Zr, Sc, Cr, Co, and Ni in isolated shale components and corresponding whole rock are presented in Table 3. The concentrations of these elements in the whole rock were normalized to their corresponding concentrations in NASC and plotted as shown (Fig. 5). Certain elements, e.g., U, Sr, Cr, and Ni are enriched in the whole rock samples while others, e.g., Ba, Th and Zr are depleted relative to NASC. The average elemental composition of Ba, Th, Zr, La, Ce, Nd, Sm, Tb, Tm, Yb, V, and Cr are higher in the immature samples than the mature and post mature samples. The post mature samples result in significantly higher concentrations of U, Sr and Co when compared to immature and mature samples. The post mature samples have a higher content of inorganic carbonate, which may account for the higher Sr content in these samples.

Concentrations of the following elements including Ba, Th, U, La, Ce, Sr, Nd, Sm, Zr, Tb, Tm, Yb, Sc, Cr, Co, and Ni in the isolated shale fractions were normalized to corresponding whole rock and plotted as shown (Fig. 6) following the work of Ohr et al. (1994). We observed an enrichment of Sr and Co relative to whole rock in a few samples but the general trend showed depletion relative to whole rock. The elements Zr and Cr are highly depleted in the sulfide and carbonate fractions relative to the whole rock. The

Table 3
REE and minor element content of whole rock and isolated rock fractions (ppm)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	∑REE
Whole rock														
USM-32	51.00	91.69	10.91	39.33	7.00	1.66	41.47	1.32	6.37	0.98	2.93	0.43	2.94	258.04
USM 44	49.40	88.27	10.74	39.52	7.46	1.66	40.51	1.24	6.44	1.00	2.87	0.45	2.99	252.56
QA 23110	37.44	81.43	9.49	35.55	8.07	2.09	42.53	1.23	5.53	0.68	1.72	0.24	1.87	227.88
QB 23073	25.83	58.20	7.56	30.50	7.52	1.70	27.37	1.16	5.49	0.83	2.10	0.30	2.05	170.59
QE 23109	62.68	121.09	14.61	51.78	11.19	1.59	56.39	2.06	10.99	1.84	5.42	0.83	5.94	346.41
QK 23411	48.49	95.84	10.95	41.28	7.43	1.76	37.24	1.22	5.55	0.80	2.21	0.32	2.30	255.41
OGS-104	57.94	115.07	13.03	45.40	7.61	1.80	41.36	1.23	5.87	0.85	2.14	0.32	2.29	294.91
OGS-106	51.22	93.40	10.83	38.29	7.81	1.67	40.03	1.17	6.05	0.94	2.51	0.40	2.72	257.02
OGS-111	27.88	43.28	5.46	19.97	3.62	0.80	18.60	0.59	3.00	0.55	1.40	0.21	1.35	126.72
OGS-753	41.25	66.18	7.57	26.78	4.40	1.05	24.58	0.63	3.62	0.59	1.68	0.22	1.88	180.42
OGS-762.5	24.21	42.70	5.43	20.29	3.51	0.80	15.16	0.51	2.70	0.43	1.17	0.17	1.12	118.20
FAA	18.28	35.45	4.05	15.10	2.81	0.84	13.91	0.50	2.56	0.45	1.17	0.17	1.18	96.46
CURA	10.13	19.81	2.25	8.35	1.33	0.32	6.68	0.21	0.94	0.11	0.36	0.05	0.33	50.86
Carbonate fraction														
USM-32	10.30	17.77	2.21	7.78	1.43	0.33	2.60	0.26	1.52	0.30	0.88	0.13	0.77	46.28
USM 44	24.10	54.21	6.55	23.16	4.44	1.08	7.23	0.72	4.18	0.81	2.19	0.32	1.99	130.97
QA 23110	11.59	30.58	4.25	18.99	5.77	1.60	6.78	0.99	5.48	0.96	2.47	0.34	2.09	91.89
QB 23073	11.78	32.85	4.69	21.63	6.80	2.04	9.18	1.32	7.86	1.43	3.73	0.52	3.16	106.99
QE 23109	43.08	87.92	9.94	33.47	6.59	0.78	24.79	1.16	6.63	1.15	3.26	0.53	3.67	222.97
QK 23411	9.03	26.01	3.68	15.77	3.34	0.86	8.15	0.60	3.30	0.58	1.54	0.22	1.42	74.51
OGS-104	30.94	69.46	9.19	37.28	7.58	1.92	22.58	1.46	8.27	1.41	3.64	0.48	3.13	197.34
OGS-106	8.12	16.18	2.34	9.58	1.90	0.48	6.72	0.42	2.39	0.43	1.15	0.17	0.97	50.85
OGS-111	10.94	17.02	2.05	7.34	1.29	0.29	4.95	0.22	1.23	0.21	0.60	0.09	0.53	46.77
OGS-753	8.83	16.36	2.05	7.87	1.65	0.33	5.61	0.26	1.29	0.22	0.54	0.08	0.50	45.58
OGS-762.5	4.41	8.97	1.12	4.23	0.82	0.20	2.81	0.15	0.79	0.13	0.36	0.05	0.34	24.39
FAA	7.18	14.38	1.60	5.67	0.90	0.23	4.26	0.16	0.88	0.15	0.45	0.07	0.42	36.37
CURA	2.39	5.82	0.66	2.25	0.33	0.08	1.39	0.07	0.30	0.05	0.13	0.02	0.14	13.63
Organic fraction														
USM-32	140.18	276.30	23.46	74.64	13.91	3.33	104.93	2.20	10.34	1.56	4.44	0.71	5.22	661.22
USM 44	329.18	604.76	59.43	191.66	30.00	5.71	324.90	5.11	24.78	3.16	9.50	1.54	11.62	1601.38
QB 23073	47.40	107.29	14.11	55.96	12.15	2.62	62.92	2.01	9.60	1.33	4.06	0.58	4.44	324.47
QE 23109	28.87	55.41	5.57	20.50	4.48	0.99	31.40	0.84	4.29	0.79	2.14	0.34	2.56	158.18
QK 23410	18.66	39.96	4.52	17.42	3.54	1.08	22.77	0.56	2.36	0.30	0.83	0.13	0.91	113.04
OGS-104	30.52	51.42	7.54	28.06	5.73	1.33	33.88	0.94	4.48	0.63	1.94	0.30	2.09	168.86
OGS-106	36.65	72.06	8.11	28.76	5.43	1.28	39.89	1.14	5.94	0.89	2.77	0.42	3.09	206.44
OGS-111	5.93	10.77	0.98	3.97	0.67	0.20	6.67	0.17	0.89	0.12	0.38	0.06	0.39	31.21
OGS-753	23.02	32.99	3.60	10.58	1.85	0.65	23.38	0.23	1.06	0.10	0.32	0.04	0.33	98.15
OGS-762.5	32.46	46.79	6.04	20.41	3.41	0.70	28.89	0.53	2.45	0.30	0.80	0.09	0.79	143.67
FAA	22.69	41.08	3.75	12.81	2.59	0.64	21.57	0.47	2.25	0.33	0.94	0.16	1.06	110.35
CURA	106.96	177.24	19.32	69.29	11.34	2.96	93.98	1.84	8.95	1.12	3.27	0.41	3.18	499.85
Sulfide fraction														
USM-32	1.86	3.51	0.43	1.61	0.28	0.06	1.27	0.04	0.17	0.02	0.06	0.01	0.07	9.39
USM 44	2.81	7.31	0.87	2.98	0.65	0.16	1.65	0.09	0.45	0.07	0.19	0.03	0.23	17.48
QA 23110	1.68	5.67	0.63	2.27	0.55	0.16	1.02	0.07	0.31	0.04	0.10	0.01	0.11	12.61
QB 23073	0.76	2.32	0.29	1.20	0.32	0.08	0.37	0.05	0.23	0.04	0.10	0.01	0.10	5.86
QE 23109	5.17	10.95	1.18	3.99	0.72	0.11	1.81	0.10	0.51	0.07	0.19	0.03	0.18	25.01
OGS-104	0.18	0.49	0.06	0.22	0.06	0.02	0.08	0.01	0.05	0.01	0.03	0.00	0.03	1.22
OGS-111	2.08	3.11	0.33	1.13	0.18	0.04	0.52	0.02	0.12	0.02	0.05	0.01	0.05	7.67
OGS-106	4.66	8.27	0.82	2.64	0.45	0.10	1.50	0.06	0.28	0.04	0.11	0.02	0.11	19.06
FAA	2.35	4.16	0.43	1.53	0.29	0.08	0.72	0.04	0.22	0.04	0.10	0.01	0.11	10.08

$Eu/Eu* = Eu_N/(Sm_N*Gd_N)^{0.5}$ and $Ce/Ce* = Ce_N/(La_N*Pr_N)^{0.5}$ where N is the NASC normalized ratio.

| Eu/Eu*	Ce/Ce*	V	Cr	Co	Ni	Sr	Y	Zr	Ba	Th	U	Ni/Co	V/Cr	V/(V+Ni)	P$_2$O$_5$
0.44	0.85	108.42	344.39	143.93	153.50	934.24	32.14	110.37	358.75	7.61	12.19	1.066	0.315	0.414	na
0.43	0.83	106.13	354.83	152.57	156.56	926.65	31.58	109.08	352.94	6.95	10.54	1.026	0.299	0.404	na
0.51	0.94	121.24	378.29	56.66	87.92	317.34	16.42	71.13	644.60	8.24	5.46	1.552	0.321	0.580	0.13
0.54	0.91	65.80	192.67	168.01	52.67	208.32	19.24	66.43	307.62	6.81	4.42	0.313	0.342	0.555	0.17
0.29	0.87	200.35	235.87	117.49	152.85	801.40	45.13	205.16	250.99	5.72	65.11	1.301	0.849	0.567	0.11
0.48	0.91	116.94	314.34	80.99	90.01	1022.81	21.48	73.24	309.65	9.05	6.91	1.111	0.372	0.565	0.15
0.46	0.91	186.50	433.41	42.68	115.81	154.19	21.22	85.86	460.96	11.95	11.22	2.714	0.430	0.617	0.33
0.43	0.86	136.33	336.10	86.85	95.81	295.91	27.53	84.10	330.39	8.49	17.75	1.103	0.406	0.587	0.35
0.44	0.76	63.69	174.76	152.26	93.65	985.45	13.67	40.09	156.38	0.45	9.31	0.615	0.364	0.405	0.14
0.46	0.82	82.88	271.21	138.64	66.19	735.46	15.41	94.83	310.18	6.77	9.77	0.477	0.306	0.556	0.41
0.50	0.81	43.26	95.70	155.08	52.16	963.08	10.40	26.63	124.62	0.72	8.71	0.336	0.452	0.453	0.39
0.61	0.90	39.83	63.89	298.42	60.68	2757.31	12.25	41.54	176.19	2.07	4.48	0.203	0.623	0.396	0.28
0.48	0.90	16.93	55.97	165.33	46.73	971.18	2.69	10.00	39.98	0.55	5.35	0.283	0.302	0.266	0.45
0.78	0.81	2.14	1.96	9.26	24.27	706.45	9.78	0.88	5.72	1.21	1.92	2.620	1.091	0.081	na
0.86	0.94	14.06	7.40	54.83	64.89	792.12	22.91	5.86	30.56	4.64	9.94	1.183	1.901	0.178	na
1.16	0.95	12.16	11.46	208.01	44.04	1612.28	25.91	1.36	137.02	5.39	7.45	0.212	1.062	0.216	na
1.17	0.96	11.84	7.62	944.16	32.27	598.82	36.12	1.20	108.33	3.16	3.57	0.034	1.553	0.268	na
0.28	0.93	18.40	4.94	61.81	46.86	1248.60	28.21	5.03	12.36	0.95	24.66	0.758	3.728	0.282	na
0.75	0.98	2.29	1.38	61.00	27.21	1738.18	18.16	0.40	40.55	0.97	1.78	0.446	1.655	0.078	na
0.67	0.90	55.17	19.30	266.28	224.35	760.52	40.68	1.92	20.13	6.98	16.07	0.843	2.858	0.197	na
0.61	0.81	15.66	8.02	74.56	36.83	295.22	13.91	1.49	6.66	0.66	3.43	0.494	1.954	0.298	na
0.53	0.78	3.73	2.52	55.95	18.17	615.04	7.73	0.15	4.92	0.60	2.38	0.325	1.477	0.170	na
0.50	0.84	4.17	3.84	65.55	19.48	577.50	6.57	0.21	53.25	1.28	1.62	0.297	1.086	0.176	na
0.58	0.88	2.22	1.96	45.68	17.91	336.21	4.96	0.20	9.43	0.33	0.95	0.392	1.132	0.110	na
0.53	0.92	5.38	2.68	95.14	17.75	1990.12	5.46	0.23	35.14	0.65	1.05	0.187	2.004	0.232	na
0.56	1.01	1.89	2.24	48.50	20.38	365.39	1.74	0.04	5.48	0.27	0.35	0.420	0.844	0.085	na
0.40	1.05	39.60	447.65	77.60	197.29	534.39	57.92	481.53	1368.84	22.97	6.35	2.542	0.088	0.167	na
0.26	0.94	61.65	206.12	25.66	271.63	406.15	97.97	965.26	1426.74	45.84	4.27	10.584	0.299	0.185	na
0.43	0.90	63.01	737.52	4.73	83.26	100.44	43.23	492.46	592.49	9.05	2.21	17.618	0.085	0.431	na
0.38	0.95	62.80	245.99	8.69	171.16	180.55	22.27	198.00	517.90	6.42	37.19	19.698	0.255	0.268	na
0.55	0.95	36.73	86.60	25.18	85.78	100.19	4.35	142.36	802.27	3.12	8.94	3.406	0.424	0.300	na
0.43	0.74	60.77	319.39	3.54	107.44	112.73	13.93	234.31	557.16	5.80	15.82	30.320	0.190	0.361	na
0.40	0.91	82.89	148.38	26.27	37.74	168.69	31.81	75.40	83.60	8.32	5.11	1.436	0.559	0.687	na
0.43	0.97	50.64	53.16	9.66	92.75	107.69	5.91	83.33	57.76	2.09	1.72	9.599	0.953	0.353	na
0.45	0.79	27.10	77.49	6.71	35.30	139.22	2.11	144.52	717.13	3.40	18.69	5.258	0.350	0.434	na
0.32	0.73	104.35	171.03	22.42	41.62	451.56	7.08	156.82	302.81	4.03	27.39	1.856	0.610	0.715	na
0.39	0.97	55.68	82.61	28.89	125.33	972.52	13.75	450.30	238.43	11.53	11.70	4.338	0.674	0.308	na
0.41	0.85	36.53	426.48	169.34	96.55	835.39	32.55	183.09	384.61	12.15	24.88	0.570	0.086	0.274	na
0.45	0.85	3.89	15.92	4.22	9.77	15.04	0.21	0.41	17.74	<0.01	1.29	2.317	0.244	0.285	na
0.71	1.02	36.45	15.67	26.74	7.83	14.82	1.40	9.64	19.08	0.61	1.16	0.293	2.326	0.823	na
0.95	1.20	10.42	5.54	7.88	5.45	10.83	1.02	3.53	20.97	0.63	0.40	0.691	1.883	0.657	na
1.11	1.08	3.83	20.44	3.04	2.87	5.39	0.58	5.82	12.94	0.15	2.43	0.943	0.187	0.572	na
0.44	0.97	14.21	43.49	10.13	24.30	22.12	0.90	12.27	16.93	0.06	11.39	2.398	0.327	0.369	na
1.15	1.05	18.08	52.33	11.97	20.62	1.36	0.10	3.71	8.89	0.03	1.07	1.723	0.345	0.467	na
0.62	0.82	4.86	28.52	3.56	4.89	11.20	0.28	0.46	13.81	<0.01	1.18	1.375	0.170	0.498	na
0.58	0.92	5.63	27.85	4.06	7.04	8.19	0.63	3.04	35.44	0.07	1.08	1.734	0.202	0.444	na
0.80	0.90	3.71	41.38	5.79	6.03	56.22	0.67	2.38	28.58	0.02	1.18	1.042	0.090	0.381	na
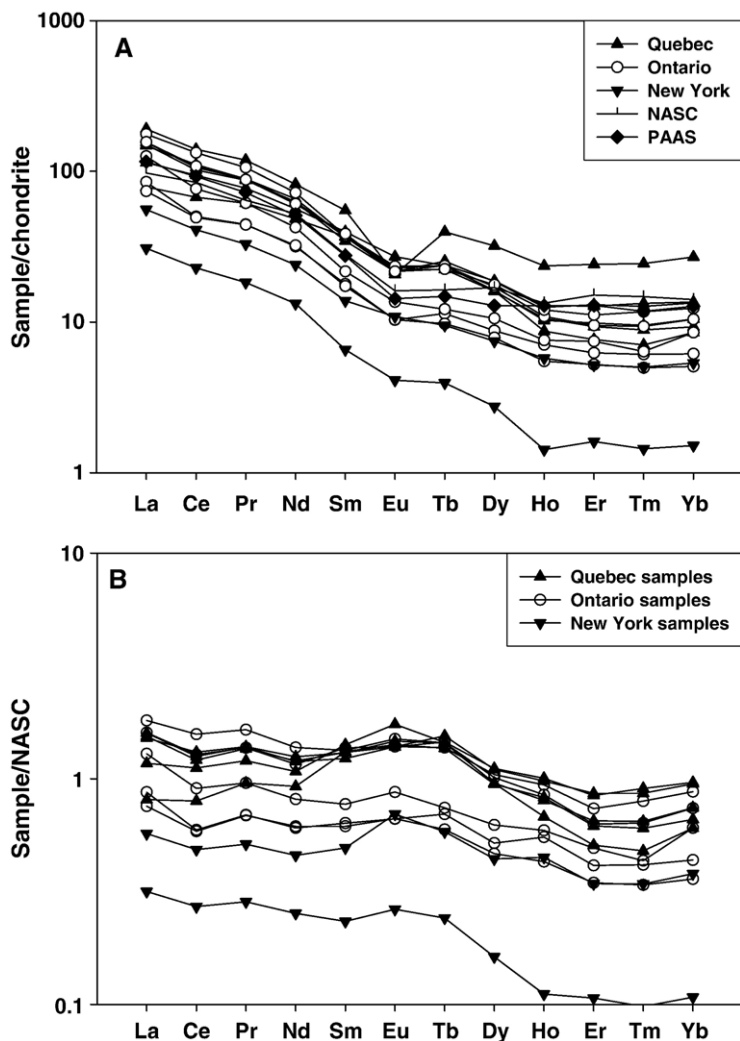
Fig. 3. Chondrite (A) and NASC (B) normalized plots of the rare earth elements in whole rock samples.

organic fraction is enriched in U, Zr, Cr, Ni, and V relative to whole rock in the following trace elements (Fig. 6). The elements U, Ni, and V tend to associate with organic matter in black shales (Patterson et al., 1987, Kaschl et al., 2000). Sr and Co are depleted in the organic fraction relative to the bulk rock. There is no clear trend of increase or decrease in the degree of enrichment/depletion of Sr, Co, Zr, and Cr with grade of thermal maturity of the samples. There is much variability in the concentration of Ba, Th, Sr, Zr, Sc, Cr, Co, and Ni in the organic fraction of these rocks when compared to their concentrations in the sulfide and carbonate fractions. We observed similar variability in the concentration of the REE in the organic fraction (Fig. 4). Relative to corresponding bulk rock composition we observed an enrichment of the elements U, Zr,

Cr, Ni, and V and a depletion of Sr, Sc and Co in the organic fractions. In general the concentration of trace elements is much lower in the sulfide fraction compared to the organic and carbonate fractions. Th and Sr show exceptionally low concentrations in this fraction while U and Cr tend to be enriched relative to other elements.

5. Discussion

5.1. Carbon, sulfur and environment of deposition

Carbon–sulfur relationships may serve as proxies for oxidation conditions during sediment deposition (Morse and Berner, 1995). Ideally carbon and sulfur tend to show a positive correlation with zero intercept in sediments deposited under normal marine conditions.
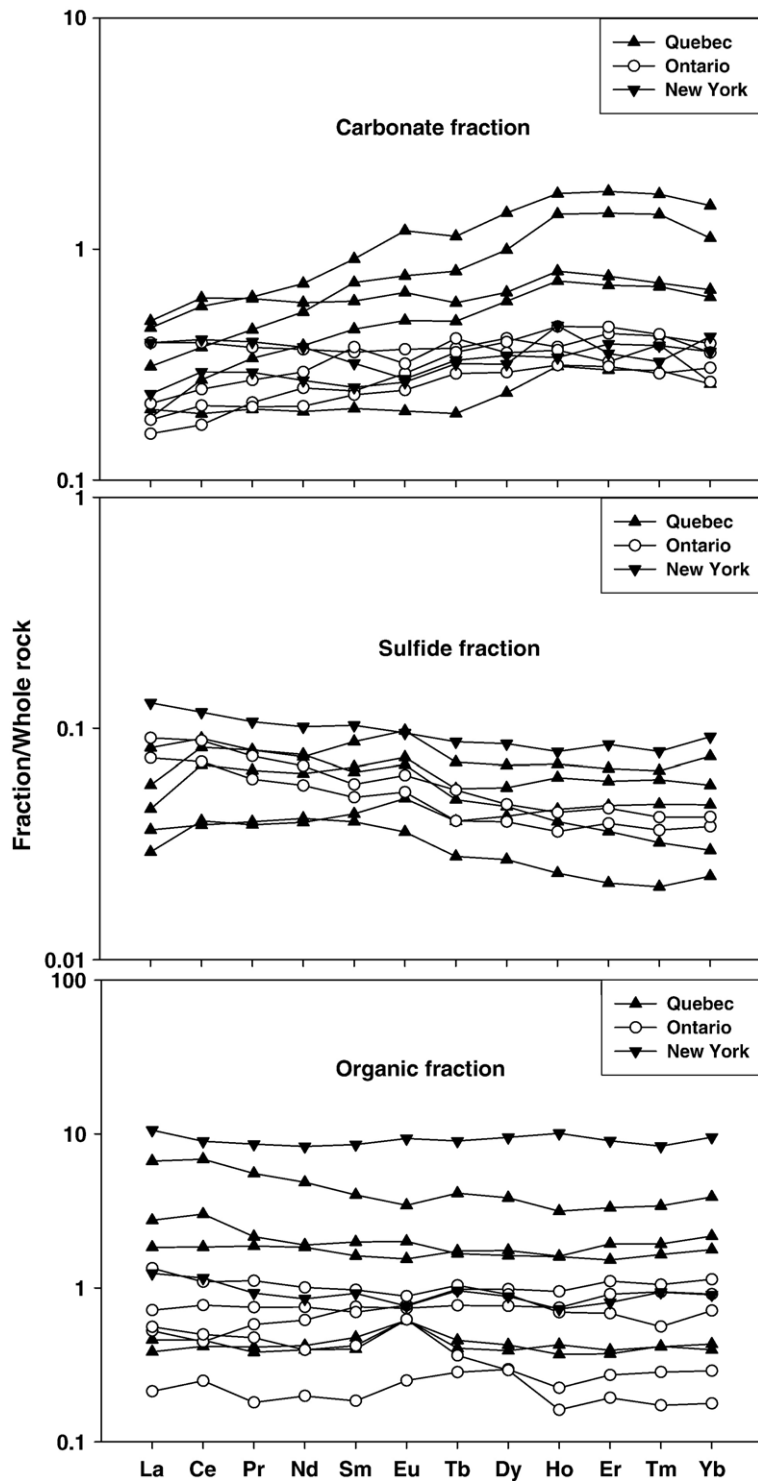
Fig. 4. Rare earth elements in isolated rock fractions (carbonate, sulfide and organic fractions) normalized to corresponding whole rock.

On the other hand, pyritic sulfur and organic carbon tend to correlate poorly in sediments deposited under anoxic conditions (Berner and Raiswell, 1983). Total sulfur and organic carbon in our samples show a poor positive correlation ($r^2 = 0.25$, $n = 13$) (Fig. 7). There is no distinct trend of increase or decrease in the sulfur and
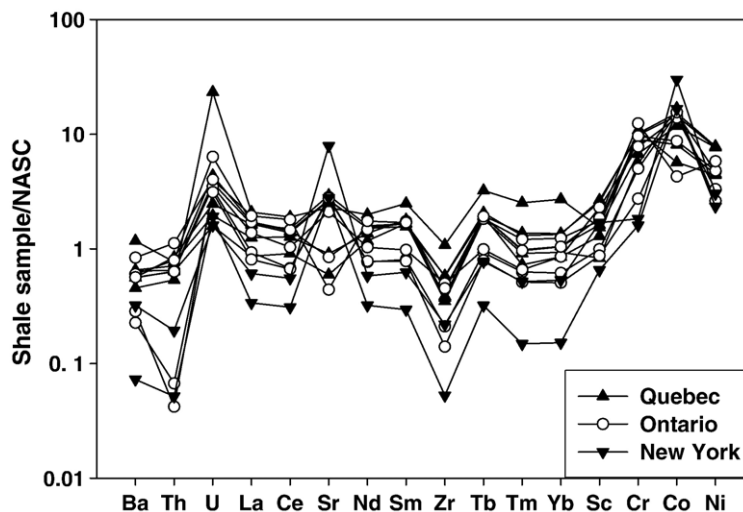
Fig. 5. Composition of minor elements including the REE in Utica shale of Quebec, Ontario and New York normalized to NASC (Gromet et al., 1984).

organic carbon content with degree of thermal maturity or with stratigraphic position of sample.

Other workers (Hannigan and Mitchell, 1994; Hannigan and Basu, 1998) using carbon–iron–sulfur systematics, suggested that the Utica Shales were deposited in normal marine to episodically oxygen deficient (anoxic) conditions. The poor correlation between organic carbon and total sulfur observed in these shales may be due to episodic anoxic events during sediment deposition or as a result of pockets of anoxia in the bulk sediment allowing the formation of diagenetic pyrite and preservation of organic matter. The amount of inorganic carbon tends to increase with increasing grade of thermal maturity with the thermally immature samples averaging 2.4 wt.% carbon; thermally mature averaging 6.5 wt.% and the post mature (New York) averaging about 5.9 wt.% inorganic carbon. Due to the small sample size and greater variability in the content of inorganic carbonate in these samples it is difficult to draw any conclusions about the concentration of inorganic carbonate and the degree of thermal maturity in our samples. It is possible that the observed differences in the inorganic carbon content in these samples may be due to differences in the original carbonate content of the shales. Nonetheless, it suffices to say that there appear to be a trend of higher carbonate content with increasing degree of thermal maturity. The inorganic carbon content in the samples can therefore be grouped into 2 categories: 0.5–5% inorganic carbon content found mainly in the immature samples and 5–10% inorganic carbon found mainly in Ontario and New York samples. The observed differences in inorganic

carbon content in these samples may be due to differences in the original carbonate content of the shales.

5.2. Partitioning of REE in whole rock and isolated shale fractions

The observed differences in the ΣREE between rocks of different thermal grades may be attributed to a number of factors including remobilization of the REE during diagenesis, sorting of REE-rich mineral phases and mixing with sediment from other sources. During early diagenesis and breakdown of sediment organic matter, trace elements including the LREE, U, Th, and Pb associated with clay mineral surfaces, Fe–Mn oxyhydroxides and or accessory minerals have the potential to migrate from the sediments into pore waters (Milodowski and Zalaskiewicz, 1991; Hannigan and Basu, 1998). As burial and sediment compaction continues, REE-rich porewaters have the potential to migrate upwards in the sediment column. Continued burial, compaction and dewatering of the sediments may lead to release of trace elements as a result of clay mineral transformations and reduction of Fe–Mn oxyhydroxides (Milodowski and Zalaskiewicz, 1991). The observed enrichment of the HREE relative to the LREE in the carbonate fraction may be related to the derived seawater signature. However the REE content of this fraction is higher than REE content of seawater (Elderfield and Greaves, 1982; Elderfield, 1988; Piepgras and Jacobsen, 1992). This suggests other sources of REE into the carbonate matrix. Assuming
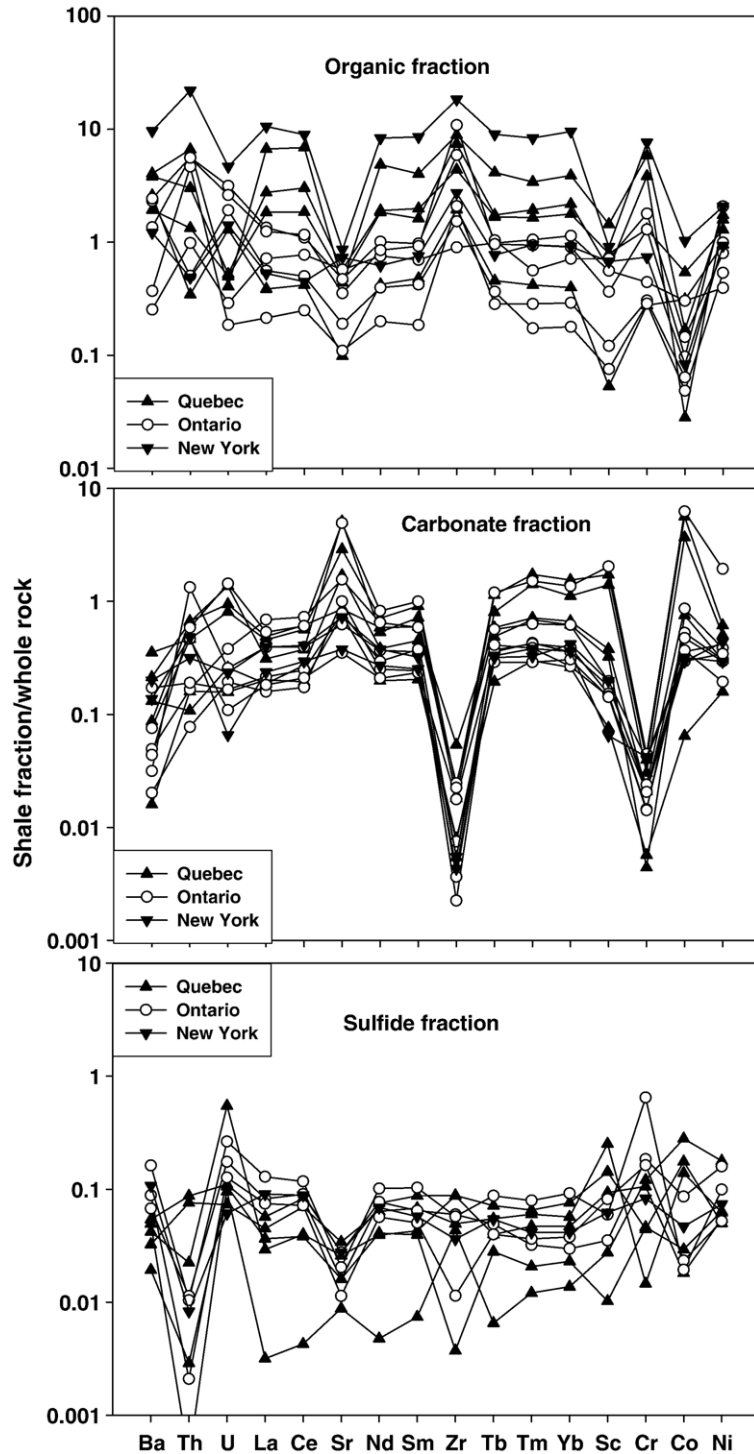
Fig. 6. Spider plots of shale fractions (carbonate, sulfide and organic fractions). Concentration of elements in fractions normalized to concentrations in corresponding whole rock. The elements are arranged in order of increasing compatibility from left being less compatible to more compatible on the right.
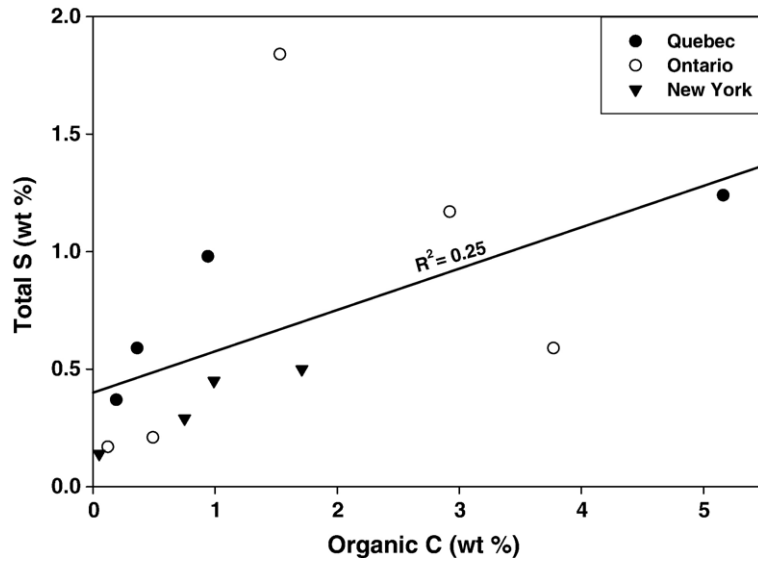
Fig. 7. Relationship between Organic carbon and total sulfur in selected samples from the USM.

that the inorganic carbonate in our samples may have been significantly increased during sediment diagenesis, then formation of diagenetic carbonate minerals in the USM may have resulted in selective movement of REE especially the HREE from sediment pore waters into this fraction. It is also possible that the amount of inorganic carbonate in the samples is a direct result of the original carbonate material in the sediments. We explain the enrichment of the HREE in the carbonate fraction as resulting from the similarity of the ionic radii of the HREE to that of the Ca^{2+} ion and the greater stability of HREE complexes and their enhanced reactivity with
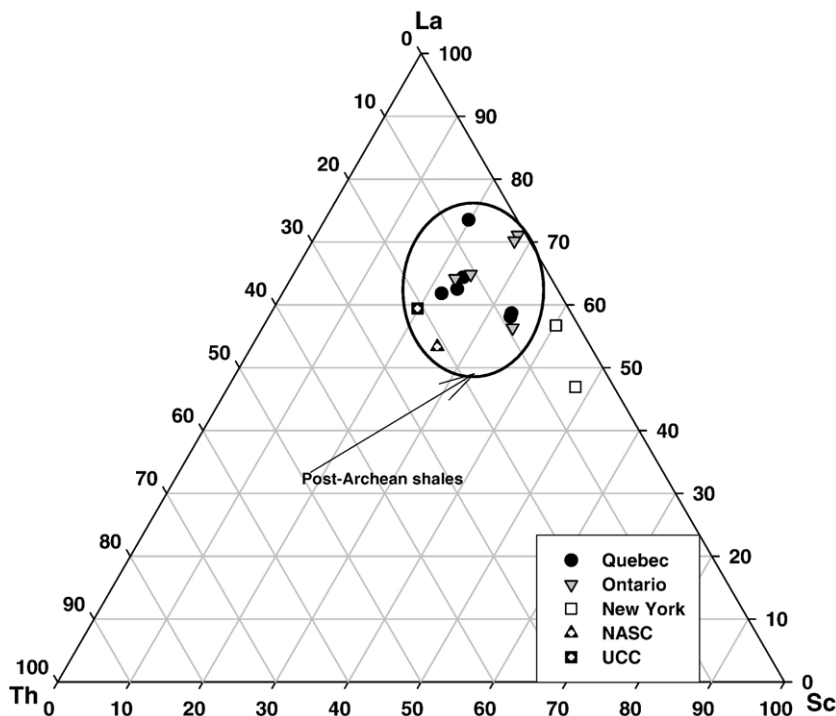
Fig. 8. La–Th–Sc ternary plot for whole rock composition of thermally immature (Quebec) thermally mature (Ontario) and thermally post mature (New York). Data for NASC and UCC are included for comparison.

anions (e.g., Elderfield and Greaves, 1982). Of interest is the absence of any significant correlation between the HREE content and the amount of inorganic carbon in the samples. The lack of a significant correlation between these two variables suggests that even though the carbonate fraction is enriched in HREE, this fraction does not control the HREE chemistry of the bulk rock and seem to indicate that, the replacement of Ca^{2+} by the HREE in the original carbonate material rather than uptake of HREE during diagenetic carbonate formation is a more plausible explanation for the enrichment of HREE in this fraction. Mass balance calculations reveal that the absolute REE content in the carbonate fraction accounts for approximately 10% of the total REE content of whole rock. In the sulfide fraction, we observe a pattern of enrichment of the light REE relative to the HREE and a slight positive Ce anomaly in a majority of the samples. Cerium unlike the other REE is readily oxidized to Ce^{4+} under oxygen rich conditions (DeBaar et al., 1985). The slight positive Ce anomaly observed in these samples may be related to later processes of sediment formation. Recent studies have shown that Ce anomaly in black shales may not be related to environment of deposition but rather to late processes of sediment formation including diagenesis (Shields and Stille, 2001). The positive Ce anomaly observed in this fraction might be process rather than source related with greater mobility of neighbouring REE, La and Pr during diagenesis or from formation of pyrite under reducing conditions.

5.3. Trace element ratios and relation to depositional environment

Rimmer (2004) used the ratios of Ni/Co, V/Cr and V/(V+Ni) proposed by earlier workers to define paleo-redox conditions of deposition for the Central Appalachian Mississippian black shales (Hatch and Leventhal, 1992; Jones and Manning, 1994). These ratios, in the case of the USM, seem to suggest deposition in changing bottom water conditions or conditions modified by later processes of rock formation. The ratio of Ni/Co in the whole rock varies for the three groups of samples (thermally immature, thermally mature and thermally post mature). This ratio is relatively higher in the immature samples compared to the mature and post mature samples. V/Cr ratios show little variation in all samples studied with an average ratio of about 0.4. V/Cr ratios less than 2 are representative of deposition under oxic conditions (Jones and Manning, 1994). Our data suggests sediment deposition under oxic conditions since the V/Cr ratio is<2. Conversely V/Cr ratios

below 2 may reflect a diagenetic overprint. There is little variation in the ratios of V/(V+Ni) between the immature and mature samples but greater variation between the latter and the post mature samples. The average V/(V+Ni) ratios in the immature and mature samples is 0.51 and 0.52, respectively, while V/(V+Ni) ratio averages 0.24 in the post mature samples. Despite the differences in the V/(V+Ni) ratios the data suggests deposition under oxic to dysoxic conditions. Comparing the ratios of Ni/Co, V/Cr and V/(V+Ni) to set thresholds values corroborate C−S data which suggests sediment deposition under normal marine conditions. However slight differences occur between these ratios in the three group of samples (e.g., Ni/Co where immature>mature>post mature) that can be related to differences in grades of thermal maturity with Co being more mobile (Rollinson, 1983).

We used La−Th−Sc and Th−Co−Zr/10 ternary plots to define sediment source and tectonic setting (Figs. 8 and 9). These proxies have been used to define different provenance fields and tectonic settings for marine sediments (Taylor and McLennan, 1985; Bhatia and Crook, 1986). On the La−Th−Sc ternary diagram (Fig. 8), all the thermally immature and thermally mature samples plot in the restricted field of Post Archean shales defined by Taylor and McLennan (1985). The thermally post mature samples plot out of this restricted field. Compositional fields of NASC and average upper continental crust (Gromet et al., 1984) are also plotted alongside our data and used for comparison. A majority of our samples plot closer to average upper continental crust than to NASC.

On the Th−Co−Zr/10 ternary diagram (Fig. 9) the USM samples plot close to the field defining samples from a volcanic island arc setting (Bhatia and Crook, 1986). Our results suggest judicious use of trace elements ratios in the study of tectonic settings of sediment deposition since these ratios are liable to change from late processes of rock formation. There is evidence to show that deposition of the USM followed the collision of a volcanic island arc with the passive margin of the North American plate (Bradley and Kidd, 1991) but the main source of siliciclastic sediment supply that to produce the USM came from weathering of Grenville basement (Andersen and Samson, 1995).

5.4. Partitioning of trace element between isolated rock fractions

We performed a mass balance calculation to determine the partitioning of Ba, Th, U, Sr, Zn, Sc, Cr, Co, Ni and the REE between different rock fractions
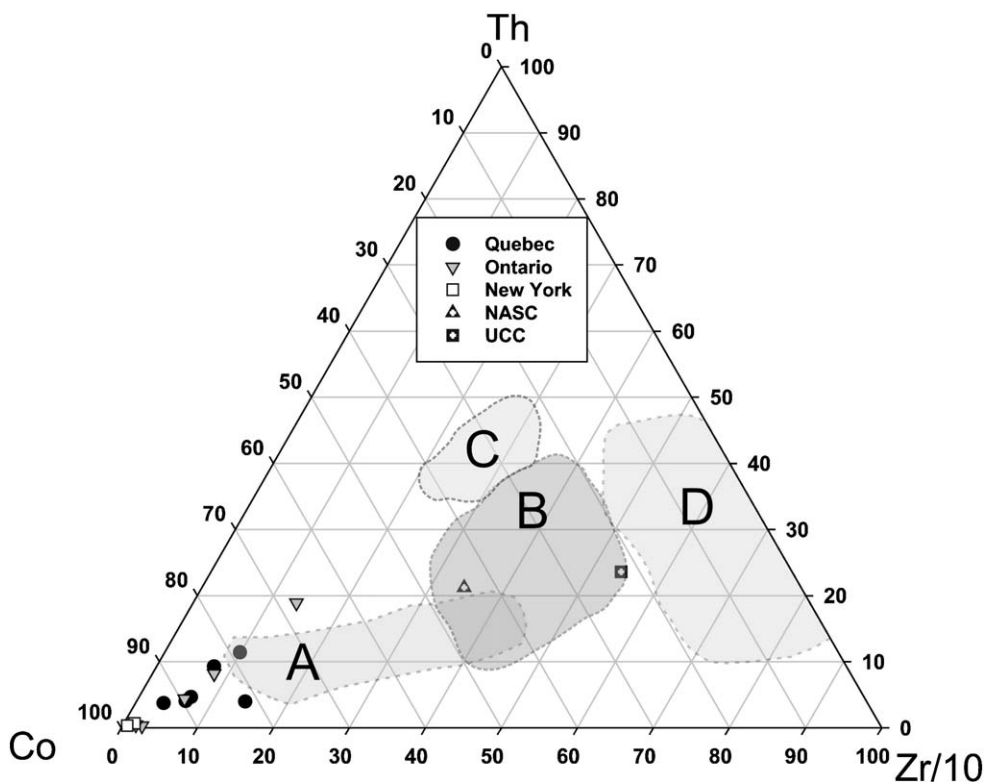
Fig. 9. Zr/10–Th–Co ternary plot for whole rock composition of thermally immature (Quebec) thermally mature (Ontario) and thermally post mature (New York). Data for NASC and UCC are included for comparison. (A) Oceanic island arc; (B) continental island arc; (C) active continental margin; (D) passive margin.

(sulfide, organic and carbonate and silicate) of the Utica shales. The silicate fraction was taken as the difference between whole rock and sum of sulfide, organic and carbonates fractions. Mass balance calculations were done using the following formula:

$$X = \frac{C_{xi}^i \times W_b^{xi}}{C_b^i} \times 100$$

Where

X = amount of particular element in a fraction (%);
C_{xi}^i = concentration of element i in fraction xi ($xi...xn$ = organic, sulfide or carbonate, silicate fraction);
C_b^i = concentration of element i in whole rock;
W_b^{xi} = percentage of fraction xi in whole rock.

We used the percentage (wt.%) of organic carbon, total sulfur, and inorganic carbon in the whole rock to calculate the trace elemental content associated with these components. Mass balance calculations show that

even though a number of trace elements tend to partition into different rock fractions, the absolute amount of these elements in the fractions are relatively low when compared to whole rock content. About 20% of whole rock elemental content is associated with the organic fraction and <10% is associated with the carbonate and sulfide fractions. The silicate fraction associated with clay minerals, as expected, dominates the trace element chemistry of the USM. However it is worth noting that the isolated components (sulfide, organic and carbonate) together constitutes less than 15 wt.% of the whole rock.

Absolute trace element content in the organic fraction is higher than in the carbonate and sulfide fractions for a majority of the samples studied. We observed significantly higher Zr contents in the organic fraction (about 10% of total Zr content in whole rock). Zr is considered to be a very immobile element during rock weathering and is usually associated with heavy refractory mineral zircons. The association of high levels of Zr with the organic fraction has not been reported for the Utica shales or for any other black shale. XRD analysis of the organic fraction was carried out to ensure that this enrichment is not an artifact of the leaching process.

Since the organic fraction was the last fraction to be obtained from the sequential extraction process, it is possible that gravity settling could have caused an enrichment of elements associated with dense refractory heavy minerals like zircon in this fraction. XRD patterns of the isolated organic fraction did not result in any peaks associated with crystalline mineral fraction. The XRD patterns resulted in the characteristic low intensity broad peak resembling a camel's hump.

Trace elements including the REE content of the organic fraction represent about 22% of the total elemental composition of the corresponding whole rock sample. This amount is higher than that associated with the sulfide and carbonate fractions. This suggests that the organic fraction exerts greater control on the whole rock REE content than the carbonate and sulfide fractions in these shales. The loss of this fraction during thermal maturation of organic matter (Raiswell and Berner, 1987) may result in loss of a substantial amount of the original REE composition especially the LREE since the LREE seems to show a slight enrichment in this fraction. This finding is important in provenance studies of organic rich sediments that use trace element composition to identify source material. However, it important to note that because black shales are made up mostly of fine grain clay sized material with low permeability; complete loss of trace elements (mass transfer) on a large scale may not be possible. However, in oil forming shales where a substantial amount of organic matter is lost as oil forms as migrates into reservoir rocks, a substantial amount of trace elements associated with fraction may be lost as well.

6. Conclusions

Separation of black shale into different fractions offers a novel approach to the study of the effects of diagenesis on the trace element geochemistry of black shales. This approach has allowed us to assess the relation between the chemistry of different rock components and whole rock. Subtle geochemical details tend to be masked during study of whole rock chemistry but become apparent from the study of individual rock fractions. These details can be very important in the study of provenance and paleoenvironment of deposition.

Mass balance calculations indicate that the carbonate and sulfide fractions each constitute less than 10% of the total elemental composition of the whole rock whereas the organic fraction make up about 20% of the total trace element chemistry of whole rock. In oil forming black shales such as the USM of Ontario and New York,

maturation and migration of organic matter may lead to loss of substantial amount of trace elements and the REE especially the LREE associated with this fraction. The elemental composition associated with the organic fraction is substantial considering that these rocks contain <5% total organic carbon. The carbonate fraction of the USM preserves the inherited signature of sea water with enrichment of the HREE relative to the LREE. However the absolute REE content of this fraction is higher than seawater content of REE, which means there is transfer of REE from host sediment into carbonate material. We observed a slightly positive europium and cerium anomaly in the sulfide fraction of the USM. The Ce anomaly is shrouded in the whole rock, but separation of the sulfide fraction enables us to identify the anomaly that may be very important in paleoenvironmental reconstruction. We were able to combine ratios of Ni/Co, V/Cr and V/(V+Ni) and C–S relationship to interpret depositional environment. These trace elements ratios combine with C–S relationship suggests deposition of the USM in a normal marine environment, consistent with findings of earlier workers.

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