

Effects of diagenesis on the Nd-isotopic composition of black shales from the 420 Ma Utica Shale Magnafacies

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Abstract

The Utica black shales were deposited in the Taconic Foreland basin ~420 Ma ago. The organic matter in these shales is of marine origin and the timing of deposition of these shales has been constrained by graptolite biostratigraphy and bentonite chronostratigraphy. Rare earth element (REE) concentrations and Nd-isotopic ratios were measured in whole rock black shales with different grades of thermal maturity from the Utica Shale Magnafacies of Quebec (immature), Ontario (mature), and New York (post mature). These measurements were also made in the organic, carbonate, and sulfide fractions of the shales, that were isolated by sequential leaching. The purpose of this study is to understand how diagenesis (thermal maturation) may affect the Nd-isotopic compositions of different components as well as the whole rock black shales.

Bulk rock REE concentrations of the Utica black shales are similar to average shales. However, these rocks show large range in ¹⁴⁷Sm/¹⁴⁴Nd (0.08–0.19) indicating diagenetic mobilization of the light-REE (LREE). Although thermal maturation of black shales may mobilize all LREE, our data indicate that mobility of La relative to Sm is greater in the mature shales compared to the post mature shales. In post mature shales, Nd is more mobile relative to Sm. Immature shales, however, show wide ranges in Sm/Nd and La/Sm that cannot be explained solely by diagenesis, implying source heterogeneity.

Whole rock black shales and their isolated components show overlapping but characteristically different Nd-isotopic compositions. If the present day Nd-isotopic compositions of black shales are mostly an artifact of diagenesis (thermal maturation), which alters the Sm/Nd ratio of the rock, it can be argued that the different components of black shales are affected to different degrees for a given diagenetic process or different diagenetic processes affect the different components. Alternatively, the varying Nd-isotopic compositions of the shale components may reflect differences in provenance of the different shale components.

Nd-isotopic composition of mature and post mature black shales of the Utica Magnafacies are controlled by thermal maturation of these rocks, as indicated by the correlation of $\epsilon_{Nd(0)}$ with various LREE ratios such as, La/Sm and Sm/Nd. However, the observed variations in the Nd isotopic composition of immature shales dominantly reflect source heterogeneity. This is also supported by the correlation of $\epsilon_{Nd(0)}$ and immobile heavy REE ratios, such as Dy/Yb, which reflect source compositions. The average $\epsilon_{Nd(0)}$ compositions of the whole rocks and separated components vary with increasing maturity, the post mature samples showing the least radiogenic Nd and the mature samples with the most radiogenic Nd isotopic compositions.

The initial Nd-isotopic compositions at 420 Ma of the Utica black shales overlap with the global seawater Nd-isotopic composition at that time. This similarity is observed for the samples with Sm/Nd ratios similar to average shales, suggesting no

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diagenetic imprint, and that the Taconic Foreland basin hosting the Utica Shale Magnafacies was probably connected to the global ocean during the time of deposition. Depleted mantle Nd model ages of the Utica black shales and their different components increase with increasing Sm/Nd. However, these model ages range from 1.6 to 2.3 Ga (average 1.9 Ga) for the samples with Sm/Nd similar to average shales. These ages indicate that the Taconic basin sediments of the Utica Shale Magnafacies were sourced from pre-Grenville-age rocks.

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1. Introduction

Rare earth element (REE) concentrations and Nd-isotopes are commonly used to study sedimentary provenance. Most commonly, these studies center around shales, which are fine grained, well-mixed representatives of the average parent material in any given depositional setting. The REE composition of the upper crust is generally represented by average shales, which show a uniform REE pattern and a narrow range of Sm/Nd ratios, typically between 0.10–0.12 (Taylor and McLennan, 1985; McLennan, 1989) due to efficient mixing of upper continental crustal sources. REEs are relatively immobile during post-depositional sedimentary processes (McLennan, 1989; McLennan et al., 1993) especially for sediments with low-organic content (<0.5 wt.% organic matter). Thus, REE compositions of shales in general remain unaltered during chemical and mechanical weathering, re-working, re-suspension, and re-deposition. Specifically, it is believed that the relative abundances of Sm and Nd do not change during deposition and very early diagenesis of shales. Several recent studies, however, (Milodowski and Zalasiewicz, 1991; Ohr et al., 1994; Lev et al., 1999; Lev and Filer, 2004) have demonstrated that diagenesis can significantly mobilize or fractionate REEs in sediments leading to their non-conservative behavior. REEs may either be gained or lost on a whole-rock scale during diagenesis. This results in disparities between the whole rock geochemical signature of shales and that of the presumed parent material. A preferential loss of the light-REEs (LREE, La–Sm) during diagenesis can significantly alter the Sm/Nd ratio and hence the Nd-isotopic signature of the sediments relative to the source rock (McLennan, 1989; Bock et al., 1994; Hannigan and Basu, 1998).

Black shales, which are dark organic-rich mudstones, are of special interest because of their importance as hydrocarbon source rocks. The exact conditions leading to the accumulation of organic matter in these rocks is debatable (Pederson and Calvert, 1990; Demaison, 1991; Pederson and Calvert, 1991) although it is well

established that organic-rich sediments forming these rocks were abundant during certain geologic times (Fischer, 1984) and preferentially preserved under certain tectonic regimes (Klemme and Ulmishek, 1991). The loss of organic matter during thermal maturation of black shales and associated remobilization of REEs may impart a diagenetic signature in black shales, which is different from the geochemical signature at the time of deposition (Raiswell and Berner, 1987). Maturation of organic matter may lead to the production of organic acids (Kawamura and Kaplan, 1987), which have the potential to alter the whole rock chemistry. The above factors may have profound effects on interpreting the provenance of these rocks and reconstructing paleodepositional environments (Mack and Awwiller, 1990; Awwiller and Mack, 1991; McDaniel et al., 1994; Anderson and Samson, 1995).

The present study focuses on black shales with different grades of thermal maturity from the Utica Shale Magnafacies of Quebec (immature), Ontario (mature), and New York (post mature). The aim of this study is to understand how thermal maturation of organic matter and production of organic acids may alter the Nd-isotopic composition of black shales. Whole rock as well as leaches representing the different shale components (siliciclastic, organic, carbonate, and sulfide), were analyzed for their REE concentrations and Nd-isotopic composition to better understand the effects of organic matter diagenesis (thermal maturation) on REE redistribution and consequently the Nd-isotopic composition of these shale components.

2. Geological setting and samples

The Utica Shales (Fig. 1) were deposited in the Taconic Foreland Basin ~420 Ma ago (Bradley and Kidd, 1991). The timing of deposition of the Utica shales has been constrained by graptolite biostratigraphy and bentonite chronostratigraphy (Goldman et al., 1994; Mitchell et al., 1994; Samson et al., 1995). The time of deposition of these shales coincided with the collision of

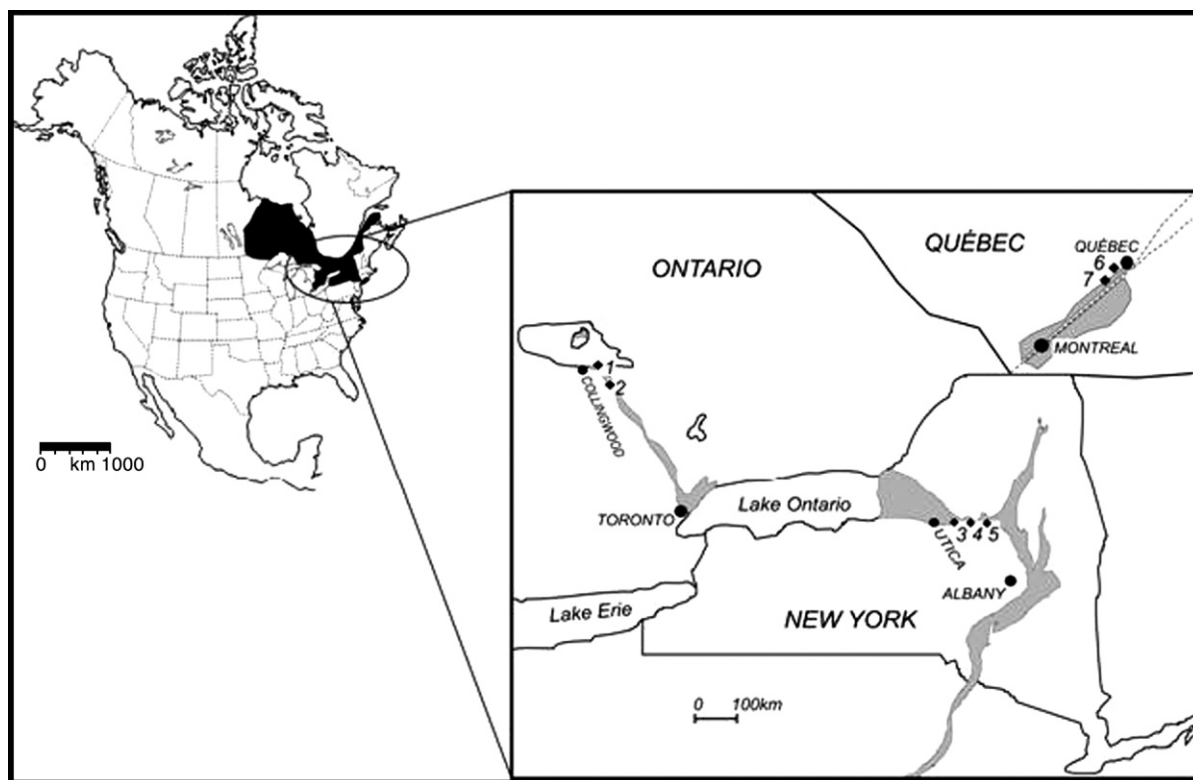


Fig. 1. Location of sample sites for the Utica shales Magnafacies of Quebec, Ontario and New York (modified from Hannigan and Basu, 1998). Sample collection sites include: Quebec, 6 and 7, Ontario, 1 and 2 and New York, 3, 4 and 5 (adopted from Abanda and Hannigan, 2006).

the Taconic island arc with the passive margin of Laurentia resulting in an increase in water levels and consequently 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 uplifted masses. Stratigraphic studies indicate that the Utica Shale sits conformably on the Trenton limestone and, at places, the two facies overlap (Brett and Baird, 2002). The organic matter in these shales is entirely of marine origin since these sediments were deposited in the middle to late Ordovician period before the proliferation of terrestrial vascular plants. The Utica Shale Magnafacies of Quebec is immature (T_{\max} 20 °C–50 °C; $R_o < 0.5$), of Ontario is mature (T_{\max} 50 °C–140 °C; R_o , 0.5–0.8), and that of New York is post mature ($T_{\max} > 140$ °C; $R_o > 1$) (Hannigan and Basu, 1998). Shale samples used in this study (Fig. 1) include drill core and trenched outcrop samples all of which are time correlative, have undergone variable degrees of diagenesis and share a common provenance. The clay mineralogy of the samples in this study is dominated by mixed layer illite/smectite (Hannigan and Basu, 1998). Minor amounts of

quartz, calcite, K-feldspar, and biotite are also present. The percentages of illite in the illite/smectite mixed clay layer vary with degree of thermal maturity with relatively higher illite contents in the New York (post mature) samples compared to the Ontario (mature) and Quebec (immature) samples. Care was taken to avoid bentonite beds that are very common in this basin (Berkley and Baird, 2002) and only samples with similar clay and organic carbon content were chosen for subsequent analysis.

3. Analytical methods

For this study, 9 whole rock samples, and 19 different sub-samples of shale components (leaches), more specifically, the organic, carbonate, and sulfide components were isolated and analyzed for trace element concentrations and Nd-isotopic compositions. We used a sequential extraction method (Abanda and Hannigan, 2006 and references therein) to isolate the different shale fractions. 25 g of finely powdered rock sample was treated with 50 ml of trace metal grade acetic acid and warmed at 60 °C in a fume hood. The mixture was stirred from time to time until completion of the

reaction, which took up to 12 hours. The supernatant solution consisting of the carbonate fraction was carefully siphoned off avoiding any agitation, and digested using ultra pure HNO_3 . The residue, which contained all the other fractions, was washed several times using 18.3 MΩ water and dried followed by treatment with ultra pure hydrofluoric acid (HF), added in 10 ml increments. The sample was stirred every 12 hours during the 48-hour reaction period and centrifuged at 3500 rpm for 20 minutes. The supernatant liquid containing the silicate fraction was decanted after centrifuging. The residue, which contained the sulfide and organic matter fraction were dried and treated with freshly prepared aqua regia solution. The sample containers were placed in a preheated hot water bath at 90 °C for three hours. The acid solution containing the sulfide fraction was extracted using 0.45 μm syringe filters. The filters were treated with 18.3 MΩ water in a beaker and agitated very gently and subsequently centri-

fuged at 10,000 rpm for about 10 minutes. Samples were washed using 18.3 MΩ water until a neutral pH (~7.0) was obtained. The residue was dried and digested at 90 °C using ultra pure HNO_3 . A few drops of trace metal grade H_2O_2 were added to this mixture to ensure complete digestion of the organic matter.

REE concentrations of the whole rocks and corresponding isolated fractions were measured by DRC-ICP-MS following EPA 6020 methodology (USEPA, 1991, 1994) at Arkansas State University. Standards containing the REE were prepared in a linear range from 1 ng/g to 1000 μg/g with all samples, standards and blanks spiked with 40 μg/g Indium (^{115}In , used to correct for instrumental drift). SDO-1 (USGS Ohio Devonian shale) was measured as an unknown to monitor external precision (better than 2% RSE for REE).

Nd-isotopic ratios were measured with a multi-collector Thermal Ionization Mass Spectrometer (TIMS, VG Sector) at the University of Rochester using

Table 1

Trace element concentrations for the Utica black shales and their components measured by DRC-ICP-MS following EPA 6020 methodology (USEPA, 1991, 1994) at Arkansas State University

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	La/Sm	Dy/Yb
1WR	51	92	10.9	39.3	7.0	1.66	41.5	1.32	6.4	0.98	2.93	0.43	2.94	0.98	7.3	2.17
4WR	25.8	58	7.6	30.5	7.5	1.70	27.4	1.16	5.5	0.83	2.10	0.30	2.05	0.46	3.44	2.68
6WR	63	121	14.6	51.8	11.2	1.59	56	2.06	11.0	1.8	5.4	0.83	5.9	1.83	5.6	1.85
3WR	37.4	81	9.5	35.6	8.1	2.09	42.5	1.23	5.5	0.68	1.72	0.24	1.87	0.42	4.64	2.95
5WR	27.9	43.3	5.5	20.0	3.62	0.80	18.6	0.59	3.00	0.55	1.40	0.21	1.35	0.45	7.7	2.22
8WR	51.2	93	10.8	38.3	7.8	1.67	40.0	1.17	6.1	0.94	2.51	0.40	2.72	0.51	6.6	2.23
9WR	41.3	66	7.6	26.8	4.40	1.05	24.6	0.63	3.62	0.59	1.68	0.22	1.88	0.20	9.4	1.93
7WR	18.3	35.4	4.05	15.1	2.81	0.84	13.9	0.50	2.56	0.45	1.17	0.17	1.18	0.21	6.5	2.18
13WR	10.1	19.8	2.25	8.3	1.33	0.32	6.7	0.21	0.94	0.11	0.36	0.05	0.33	0.12	7.6	2.83
1OM	140	276	23.5	75	13.9	3.33	105	2.20	10.3	1.56	4.44	0.71	5.2	1.85	10.1	1.98
4OM	47.4	107	14.1	56	12.1	2.62	63	2.01	9.6	1.33	4.06	0.58	4.44	3.45	3.90	2.16
6OM	28.9	55	5.6	20.5	4.48	0.99	31.4	0.84	4.29	0.79	2.14	0.34	2.56	0.44	6.4	1.67
3OM	4530	7190	883	2781	344	49.3	3999	63.9	307	41.9	133	23.0	162	36.6	13.2	1.89
5OM	5.9	10.8	0.98	3.97	0.67	0.20	6.7	0.17	0.89	0.12	0.38	0.06	0.39		8.9	2.27
8OM	36.6	72	8.1	28.8	5.4	1.28	39.9	1.14	5.9	0.89	2.77	0.42	3.09	1.23	6.7	1.92
9OM	23.0	33.0	3.60	10.6	1.85	0.65	23.4	0.23	1.06	0.10	0.32	0.04	0.33		12.4	3.17
7OM	22.7	41.1	3.75	12.8	2.59	0.64	21.6	0.47	2.25	0.33	0.94	0.16	1.06	0.56	8.8	2.12
13OM	107	177	19.3	69.3	11.3	2.96	94	1.84	9.0	1.12	3.27	0.41	3.18	0.29	9.4	2.82
1S	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	0.01	6.7	2.55
4S	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	0.01	2.35	2.39
8S	4.66	8.3	0.82	2.64	0.45	0.10	1.50	0.06	0.28	0.04	0.11	0.02	0.11	0.01	10.4	2.53
1C	10.3	17.8	2.21	7.8	1.43	0.33	2.60	0.26	1.52	0.30	0.88	0.13	0.77	0.22	7.2	1.99
6C	43.1	88	9.9	33.5	6.6	0.78	24.8	1.16	6.6	1.15	3.26	0.53	3.67	0.90	6.5	1.80
3C	11.6	30.6	4.25	19.0	5.8	1.60	6.8	0.99	5.5	0.96	2.47	0.34	2.09	0.47	2.01	2.62
8C	8.1	16.2	2.34	9.6	1.90	0.48	6.7	0.42	2.39	0.43	1.15	0.17	0.97	0.34	4.28	2.48
9C	8.8	16.4	2.05	7.9	1.65	0.33	5.6	0.26	1.29	0.22	0.54	0.08	0.50	0.06	6.3	2.58
7C	7.2	14.4	1.60	5.7	0.90	0.23	4.26	0.16	0.88	0.15	0.45	0.07	0.42	0.05	8.0	2.09
13C	2.39	5.8	0.66	2.25	0.33	0.08	1.39	0.07	0.30	0.05	0.13	0.02	0.14	0.01	7.1	2.15

The concentrations are shown in μg/g (ppm). Analytical uncertainties are better than 2% RSE.

previously established procedures (Basu et al., 1990). Powdered whole rock samples along with the isolated components were digested in acid mixtures of HF, HNO₃ and HCl followed by ion chromatography to extract Nd. The laboratory procedural blanks are less than 200 pg for Nd.

4. Geochemical results

REE concentrations of the whole rock and different shale components are given in Table 1. The sum of rare earth elements (Σ REE) in the whole rock samples ranges between 50 ppm and 297 ppm. Immature samples have the highest REE concentrations while

lower REE content is associated with the post-mature samples (Abanda and Hannigan, 2006). These results are consistent with other studies of the Utica shales (Bock et al., 1994; Hannigan and Basu, 1998). Mass balance calculations indicate that the carbonate and sulfide fractions each contribute less than 10% of the total REE budget of the rock while the organic fraction contributes about 20%. However, it is worth noting that the isolated fractions (sulfide, organic and carbonate) constitute less than 15% by weight of the whole rock while the silicate fraction makes up the remaining bulk of the rock (Abanda and Hannigan, 2006).

The samples have a large range of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (0.08–0.19, Table 2) when compared to average shales,

Table 2

Nd isotopic composition of the Utica black shales and their components, and their respective depleted mantle Nd model ages

Sample #	Description (Fraction/maturity/location)	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}(0)^a$	$\varepsilon_{\text{Nd}(0)}^b$	$\varepsilon_{\text{Nd}(T)}^c$	T_{DM}^d (Ga)
1WR	Whole rock, immature, Quebec	7.0	39.3	0.11	0.511852	−15.3	−10.8	2.0
4WR	Whole rock, immature, Quebec	7.5	30.5	0.16	0.511759	−17.1	−15.0	3.6
6WR	Whole rock, immature, Quebec	11.2	51.8	0.14	0.512178	−9.0	−5.8	1.9
3WR	Whole rock, immature, Ontario	8.1	35.6	0.14	0.511655	−19.2	−16.3	3.2
5WR	Whole rock, mature, Ontario	3.62	20.0	0.11	0.511775	−16.8	−12.4	2.1
8WR	Whole rock, mature, Ontario	7.8	38.3	0.13	0.511978	−12.9	−9.3	2.1
9WR	Whole rock, mature, Ontario	4.4	26.8	0.10	0.511906	−14.3	−9.3	1.7
7WR	Whole rock, postmature, New York	2.81	15.1	0.12				
13WR	Whole rock, postmature, New York	1.33	8.3	0.10	0.511548	−21.3	−16.1	2.2
1OM	Organic, immature, Quebec	13.9	74	0.12	0.511985	−12.7	−8.5	1.9
4OM	Organic, immature, Quebec	12.1	56	0.14				
6OM	Organic, immature, Quebec	4.48	20.5	0.14	0.511998	−12.5	−9.4	2.3
3OM	Organic, immature, Ontario	3.44	27.8	0.08	0.511436	−23.4	−17.1	1.9
5OM	Organic, mature, Ontario	0.67	3.97	0.11	0.511919	−14.0	−9.2	1.7
8OM	Organic, mature, Ontario	5.4	28.8	0.12	0.511895	−14.5	−10.4	2.0
9OM	Organic, mature, Ontario	1.85	10.6	0.11	0.511829	−15.8	−11.2	2.0
7OM	Organic, postmature, New York	2.59	12.8	0.13	0.511898	−14.4	−10.7	2.2
13OM	Organic, postmature, New York	11.3	69	0.10	0.511479	−22.6	−17.6	2.3
1S	Sulfide, immature, Quebec	0.28	1.61	0.11	0.511950	−13.4	−8.7	1.7
4S	Sulfide, immature, Quebec	0.32	1.20	0.17	0.511728	−17.8	−16.3	4.8
8S	Sulfide, mature, Ontario	7.8	38.3	0.13	0.511873	−14.9	−11.3	2.3
1C	Carbonate, immature, Quebec	1.43	7.8	0.12	0.512044	−11.6	−7.3	1.7
6C	Carbonate, immature, Quebec	6.6	33.5	0.12	0.512244	−7.7	−3.8	1.6
3C	Carbonate, immature, Quebec	5.8	19.0	0.19	0.511633	−19.6	−19.4	10.5
8C	Carbonate, mature, Ontario	1.89	9.6	0.13	0.512091	−10.7	−6.8	1.8
9C	Carbonate, mature, Ontario	1.65	7.9	0.13	0.511996	−12.5	−9.1	2.2
7C	Carbonate, postmature, New York	1.29	7.3	0.11	0.511839	−15.6	−11.0	1.9
13C	Carbonate, postmature, New York	0.08	0.33	0.16	0.511602	−20.2	−18.2	4.3

^a Measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$. Uncertainties for the measured $^{143}\text{Nd}/^{144}\text{Nd}$ were less than 3 in the 5th decimal place. La Jolla Nd-standard analyzed during the course of this study yielded $^{143}\text{Nd}/^{144}\text{Nd}=0.511852\pm 24$ ($2\sigma_{\text{mean}}$) ($n=6$) where the two standard errors correspond to the 5th decimal place.

^b $\varepsilon_{\text{Nd}(0)}$ and $\varepsilon_{\text{Nd}(T)}$ were calculated using the present day Bulk Earth (CHUR) value of $^{143}\text{Nd}/^{144}\text{Nd}=0.512638$ and $^{147}\text{Sm}/^{144}\text{Nd}=0.1967$. The $\varepsilon_{\text{Nd}(0)}$ values represent the deviation of $^{143}\text{Nd}/^{144}\text{Nd}$ in parts per 10^4 from the present day CHUR value.

^c $T=420$ Ma (see text for details).

^d Depleted mantle Nd model ages (T_{DM}) were calculated using $\varepsilon_{\text{Nd}(0)}=+10$ and $^{147}\text{Sm}/^{144}\text{Nd}=0.2136$ for the depleted mantle.

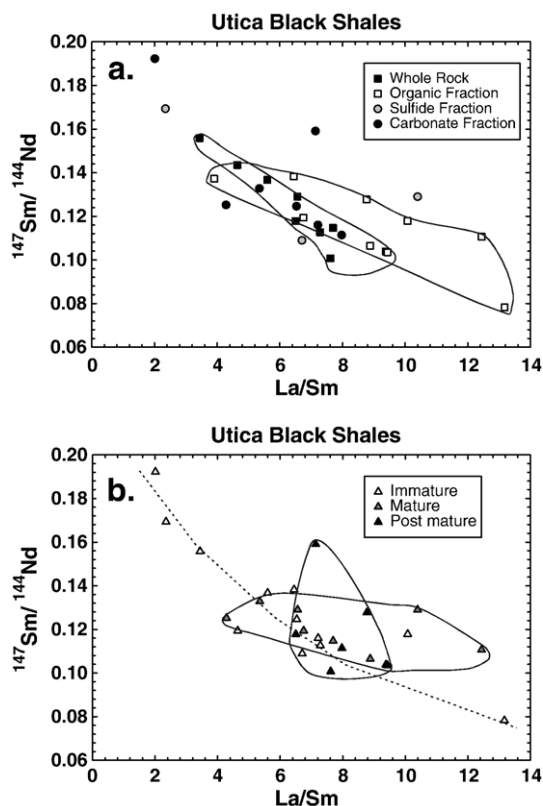


Fig. 2. (a) A plot showing the negative correlation between $^{147}\text{Sm}/^{144}\text{Nd}$ and La/Sm in the whole rock Utica shales and their isolated fractions. While the sulfide and carbonate fractions show some scatter in this correlation diagram, the whole rock samples and the organic fractions show good correlations. Note that the whole rock samples show a steeper slope compared to the organic fraction in this correlation diagram. (b) The same variation as in (a) between $^{147}\text{Sm}/^{144}\text{Nd}$ and La/Sm in the Utica shales and their components, but based on thermal maturity of the samples. Mature shales and their components show large variations in La/Sm associated with small changes in $^{147}\text{Sm}/^{144}\text{Nd}$ while post mature shales and their components show wide variations in $^{147}\text{Sm}/^{144}\text{Nd}$ with small changes in La/Sm . Immature samples show the maximum observed variations in both La/Sm and $^{147}\text{Sm}/^{144}\text{Nd}$ with slopes intermediate between the mature and post mature shales.

which have $^{147}\text{Sm}/^{144}\text{Nd}$ ratios ranging from 0.1–0.12 (Taylor and McLennan, 1985). As expected, all the samples of the present study including whole rock shales as well as their separated components show an overall negative correlation between $^{147}\text{Sm}/^{144}\text{Nd}$ and La/Sm (Fig. 2a), which vary from 2.0–12.4 (Table 1). The best correlation is observed in the whole rock samples and the organic fraction. As indicated by the outlined fields, the whole rock samples show a steeper slope compared to the organic fraction in this correlation diagram (Fig. 2a). When grouped in terms of thermal maturity, immature, mature and post mature samples

show different slopes in a $^{147}\text{Sm}/^{144}\text{Nd}$ versus La/Sm correlation diagram (Fig. 2b).

Present day Nd isotopic composition of the whole rock samples and their fractions are shown in Table 2. $\epsilon_{\text{Nd}(0)}$

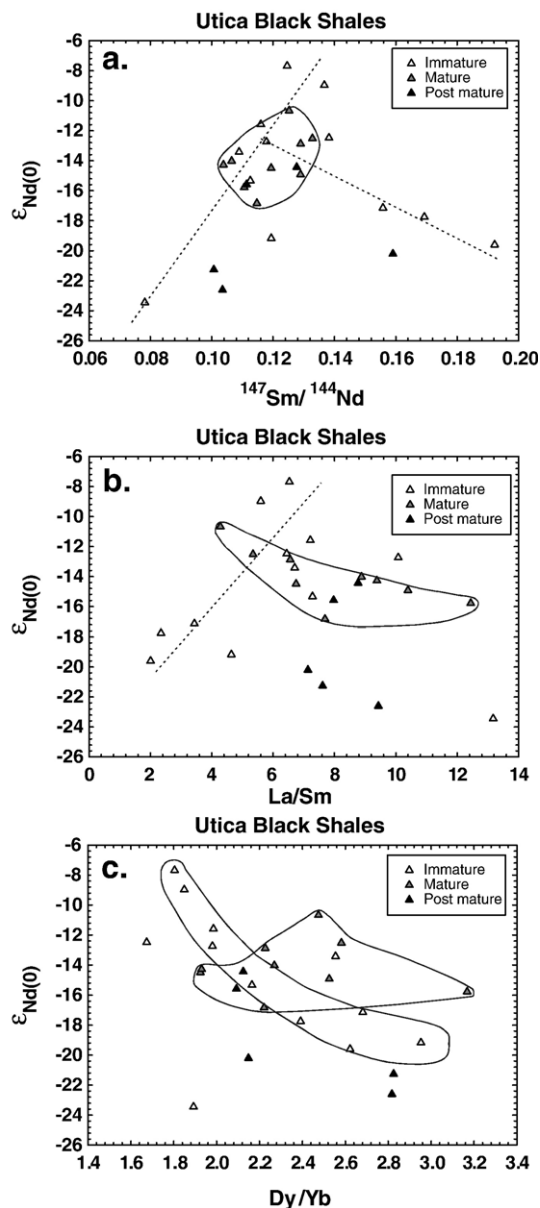


Fig. 3. Variations of present day ϵ_{Nd} with $^{147}\text{Sm}/^{144}\text{Nd}$, La/Sm and Dy/Yb , respectively, in the Utica black shales. $\epsilon_{\text{Nd}(0)}$ of the mature samples show a slightly positive correlation with $^{147}\text{Sm}/^{144}\text{Nd}$ (a), a shallow negative correlation with La/Sm (b) and shows a flat pattern when plotted against Dy/Yb (c). In contrast, $\epsilon_{\text{Nd}(0)}$ of most of the immature samples show a positive correlation with La/Sm (b) and a negative correlation with Dy/Yb (c). The immature samples show two distinct trends in the $\epsilon_{\text{Nd}(0)}$ versus $^{147}\text{Sm}/^{144}\text{Nd}$ variation diagram (a). $\epsilon_{\text{Nd}(0)}$ of the post mature samples show a slightly negative trend when plotted against Dy/Yb (c) while no distinct trend is observed in a–b.

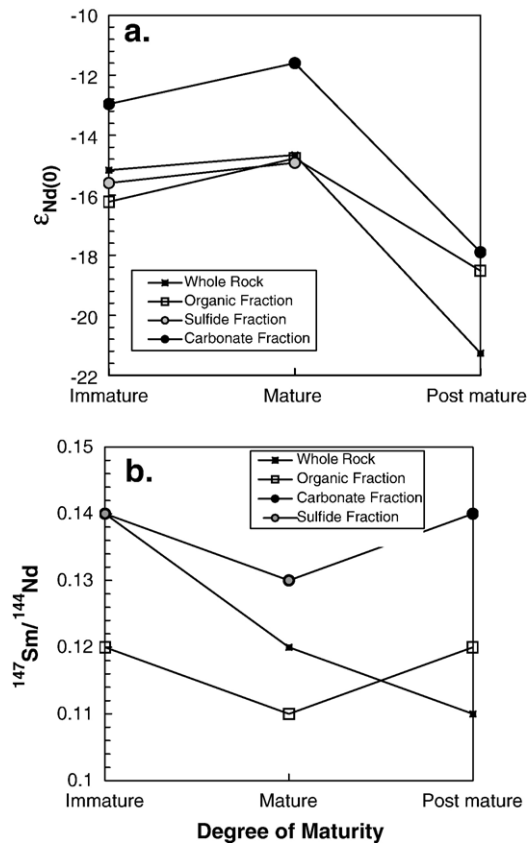


Fig. 4. Variations in the average present day Nd-isotopic compositions (a) and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (b) of the black shales, respectively, plotted against increasing maturity. Post mature samples have the least radiogenic Nd-isotopic compositions while the average matured shales show more radiogenic Nd-isotopic compositions when compared to the immature samples. The average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the different fractions show opposite effects as expected, except for the whole rock samples whose average $^{147}\text{Sm}/^{144}\text{Nd}$ ratio decreases with progressively increasing maturity of the shales.

values for the whole rock samples range from -19.2 to -9.0 (average -15.2) for the immature shales, from -16.8 to -12.9 (average -14.7) for the mature shales and is -21.3 for the post-mature shales. The $\epsilon_{\text{Nd}(0)}$ values for the organic fractions range from -23.4 to -12.5 (average -16.2) for the immature shales, from -15.8 to -14.0 (average -14.8) for the mature shales and from -22.6 to -14.4 (average -18.5) for the post mature shale samples. The carbonate fractions have $\epsilon_{\text{Nd}(0)}$ values ranging from -19.6 to -7.7 (average -13) for the immature shales, from -12.5 to -10.7 (average -11.6) for the mature shales and from -20.2 to -15.6 (average -17.9) for the post-mature shales.

Variations of present day ϵ_{Nd} with $^{147}\text{Sm}/^{144}\text{Nd}$, La/Sm and Dy/Yb are shown in Fig. 3. $\epsilon_{\text{Nd}(0)}$ of the mature samples show a slightly positive correlation with

$^{147}\text{Sm}/^{144}\text{Nd}$ (Fig. 3a), a shallow negative correlation with La/Sm (Fig. 3b) and shows a flat pattern when plotted against Dy/Yb (Fig. 3c). In contrast, $\epsilon_{\text{Nd}(0)}$ of most of the immature samples show a positive correlation with La/Sm (Fig. 3b) and a negative correlation with Dy/Yb (Fig. 3c). The immature samples show two distinct trends in the $\epsilon_{\text{Nd}(0)}$ versus $^{147}\text{Sm}/^{144}\text{Nd}$ variation diagram (Fig. 3a). $\epsilon_{\text{Nd}(0)}$ of the post mature samples show a slightly negative trend when plotted against Dy/Yb (Fig. 3c) while no distinct trend is observed in Fig. 3a and b.

Average $\epsilon_{\text{Nd}(0)}$ of the whole rocks and the separated components vary with increasing maturity (Fig. 4a) with the post mature samples having the least radiogenic Nd isotopic compositions and the mature samples having the most radiogenic isotopic composition. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the separated components show an opposite trend (Fig. 4b) with the post mature samples having the highest $^{147}\text{Sm}/^{144}\text{Nd}$ ratios and the mature samples having the lowest average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. However, the whole rocks show a different trend with the post mature samples having the lowest average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (Fig. 4b). Initial ϵ_{Nd} values at 420 Ma for samples with Sm/Nd ratios similar to normal shales range from -16.1 to -3.8 and overlap with the global seawater Nd isotope evolution curve (Fig. 5) (Keto and Jacobsen, 1988).

Depleted mantle model ages (T_{DM}) for the whole rock samples range from 1.9–3.6 Ga for the immature samples, from 1.7–2.1 Ga for the mature samples and is about 2.2 Ga for the post-mature shales. For the separated rock fractions, the T_{DM} values range from 1.6 Ga to 4.0 Ga and higher (Table 2). Higher T_{DM}

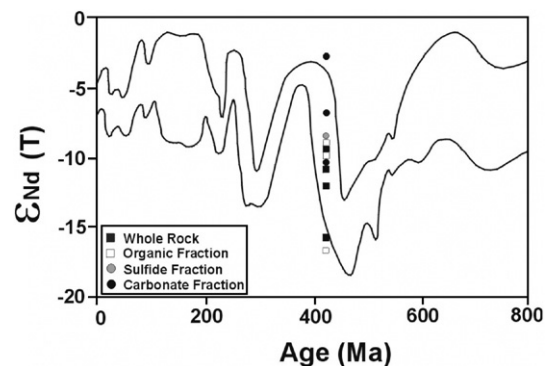


Fig. 5. Initial ϵ_{Nd} values at 420 Ma for the Utica black shales and their components, which have Sm/Nd ratios similar to average shales, are plotted in relation to the global seawater Nd-isotopic variation curve with time. The correspondence of the black shale data with the global seawater Nd isotopic composition at that time is noteworthy. This observation suggests that the Taconic Foreland Basin, which hosts the Utica shales, was connected to the global oceans at that time.

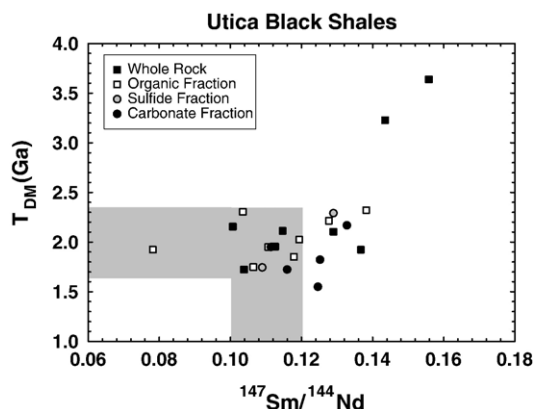


Fig. 6. Depleted mantle Nd model ages (T_{DM}) of the Utica black shales and their various components increase with increasing Sm/Nd ratios. Also shown for comparison is the range of the Sm/Nd ratios for normal shales (shaded region). T_{DM} for the Utica shale samples with normal Sm/Nd ratios indicate pre-Grenville-age sources for these shales.

values correspond to higher $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (Fig. 6). For samples with Sm/Nd ratios similar to normal shales, T_{DM} values range from 1.6–2.3 Ga (average 1.9 Ga).

5. Discussion

The extremely uniform REE pattern of normal shales is the result of efficient mixing of upper continental crustal sources. Hence, shales have a narrow range of Sm/Nd ratios, typically between 0.10–0.12, similar to the average upper crust (Taylor and McLennan, 1985; McLennan, 1989). Diagenesis can mobilize REEs in sediments leading to their non-conservative behavior (Milodowski and Zalasiewicz, 1991; Ohr et al., 1994; Lev et al., 1999; Lev and Filer, 2004). Although the whole rock REE concentrations of the Utica shales are similar to average shales (Abanda and Hannigan, 2006), the large range of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (0.08–0.19) observed in the Utica shales indicates post-depositional mobilization of light-REE (LREE) in these shales. Differences in REE contents between rocks of different thermal grades may be attributed to a number of factors including remobilization of REEs during early diagenesis, sorting of REE-rich mineral phases and mixing with sediments from other sources.

It has been argued (Bros et al., 1992; Lev et al., 1999) that as a consequence of diagenetic reactions, REEs are redistributed on a mineralogical scale and that the REEs, as well as uranium, and their associated isotopic systems (Sm–Nd and U–Pb) can be sensitive indicators of diagenetic overprint rather than the source area and depositional conditions. There is, however, a lack of

consensus as to whether mineral-scale changes can alter the whole rock chemistry or not. Milodowski and Zalasiewicz (1991) argues that low temperature processes affect the chemistry of organic rich sediments but the overall rock chemistry is not altered since this change is rather on a small mineralogical scale. Other studies have also indicated that processes of sedimentation and diagenesis do not significantly fractionate these elements and as a result the Sm–Nd isotopic system can be used for both age determination and reconstructing paleodepositional environment (Chaudhuri and Cullers, 1979; Stille and Clauer, 1986; Ugidos et al., 1997). Sedimentary facies should not affect the REE distribution in rocks since heavy minerals, which dominate the REE budget in sedimentary rocks, are sorted out before black shale deposition.

Whole rock and separated components of black shales of the present study show a large range of $^{147}\text{Sm}/^{144}\text{Nd}$ (0.08–0.19, Table 2) compared to average shales (0.1–0.12) (Taylor and McLennan, 1985). As shown in Fig. 2a, the samples of the present study show an overall negative correlation between $^{147}\text{Sm}/^{144}\text{Nd}$ and La/Sm. While the sulfide and carbonate fractions show some scatter in this correlation diagram, the whole rock samples and the organic fractions show good correlations. As indicated by the outlined fields in Fig. 2a, the whole rock samples show a steeper slope compared to the organic fraction in this correlation diagram. Variations of La/Sm in black shales and their components are controlled by source compositions as well as the degree of diagenesis (thermal maturation), which mobilizes LREE. Hence, the different slopes of the whole rock and the organic fraction could either indicate differences in source compositions of the organic fraction and bulk of the whole rock (mostly silicate) or different degrees of diagenesis affecting the organic fraction and the bulk of the whole rock.

If thermal maturity controls LREE mobilization in black shales, rocks with different degrees of thermal maturation should show different slopes in a $^{147}\text{Sm}/^{144}\text{Nd}$ versus La/Sm correlation diagram. In this correlation diagram (Fig. 2b), matured shales and their components show large variations in La/Sm associated with small changes in $^{147}\text{Sm}/^{144}\text{Nd}$, while post mature shales and their components show wide variations in $^{147}\text{Sm}/^{144}\text{Nd}$ with small changes in La/Sm. Immature samples show the maximum observed variations in both La/Sm and $^{147}\text{Sm}/^{144}\text{Nd}$ with slopes intermediate between the mature and post mature shales as shown in Fig. 2b. This observation indicates that the mobility of La relative to Sm is greater in the mature shales compared to the post mature shales in which, mobility of Nd relative to Sm is

much higher. The wide variations in both La/Sm and $^{147}\text{Sm}/^{144}\text{Nd}$ in the immature shales possibly reflect source heterogeneity.

It is interesting to note that the different components of black shales have overlapping but different Nd-isotopic compositions. What controls the observed variation in $\epsilon_{\text{Nd}(0)}$ in the Utica black shales and in their different components as observed in the present study? Are these isotopic variations an artifact of source heterogeneity of the different shale components or does thermal maturation effect the Nd-isotopic compositions? If the measured Nd-isotopic compositions of black shales are an artifact of diagenesis altering the Sm/Nd ratio of the rock, observed variations in $\epsilon_{\text{Nd}(0)}$ in the different shale components must indicate different degrees of diagenetic alteration of the shale components by the same process. Alternatively, different diagenetic processes could have affected the different shale components. However, as shown in Fig. 3a, $\epsilon_{\text{Nd}(0)}$ does not vary systematically with changes in $^{147}\text{Sm}/^{144}\text{Nd}$. If thermal maturation of black shales controlled the Nd-isotopic composition of these rocks, $\epsilon_{\text{Nd}(0)}$ should have been positively correlated with $^{147}\text{Sm}/^{144}\text{Nd}$. Only the mature shale samples of this study show a slight positive correlation between $\epsilon_{\text{Nd}(0)}$ and $^{147}\text{Sm}/^{144}\text{Nd}$. We argue that the lack of correlation of $\epsilon_{\text{Nd}(0)}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ in the immature samples possibly indicates source heterogeneity. In addition, the immature shales were possibly derived from multiple sources with contrasting Nd isotopic compositions as shown in Fig. 3a. This is also supported by the wide range in the initial Nd-isotopic compositions of the immature shales at 420 Ma ($\epsilon_{\text{Nd}(T)} = -10.8$ to -3.8 ; Table 2) which show $^{147}\text{Sm}/^{144}\text{Nd}$ similar to normal shales.

If the Nd isotopic compositions of the black shales are solely dependent on LREE mobilization during diagenesis, a negative correlation between $\epsilon_{\text{Nd}(0)}$ and La/Sm should also be observed. This is clearly seen in mature shales (Fig. 3b) indicating that the Nd isotopic compositions of mature shales reflect a diagenetic imprint. However, immature shales show a perceptible positive correlation between $\epsilon_{\text{Nd}(0)}$ and La/Sm (Fig. 3b). This indicates that the Nd isotopic compositions of immature shales reflect source characteristics. Heavy rare earth elements (HREE, Dy–Yb) are not mobilized by diagenesis and hence variations in Dy/Yb (Fig. 3c) are indicative of their source compositions. Nd-isotopic compositions of the immature samples are negatively correlated with Dy/Yb (Fig. 3c) indicating that radiogenic Nd is derived from HREE-depleted sources. The mature shales and their components have a narrow range of $\epsilon_{\text{Nd}(0)}$ although their Dy/Yb ratios show large variations (Fig. 3c). This

relatively flat pattern indicates that for mature shales, diagenetic effects dominate over source heterogeneity in controlling the Nd-isotopic composition.

Post mature shales have the least radiogenic average present-day Nd-isotopic compositions (Fig. 4a) while the mature samples show more radiogenic average Nd-isotopic compositions compared to the immature samples. The same diagenetic process could not have produced these signatures, implying that diagenesis of black shales is a multi-stage process involving different diagenetic agents. The average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the different fractions show (Fig. 4b) opposite effects as expected from the discussion above. However, the average whole rock $^{147}\text{Sm}/^{144}\text{Nd}$ ratio changes linearly with increasing maturity of the shales, with the post mature samples having the lowest average $^{147}\text{Sm}/^{144}\text{Nd}$ ratios and the immature shales showing the highest values (Fig. 4b). This relationship indicates that for the post mature samples, the Sm/Nd ratio of the siliciclastic (clay) fraction controls the whole rock Nd-isotopic composition.

For samples with Sm/Nd ratios in the range of normal shales (Taylor and McLennan, 1985), the initial Nd isotopic composition at 420 Ma overlaps with the global seawater Nd-isotopic composition (Fig. 5) (Keto and Jacobsen, 1988). The organic matter in these shales is entirely marine in origin since these sediments were deposited in the middle to late Ordovician period before the proliferation of vascular land plants. The Nd-isotopic composition of the organic fraction therefore appears to truly represent the Nd-isotopic composition of the ambient seawater. Our data thus suggest that the Taconic Foreland Basin, the depositional setting of the Utica Shale Magnafacies, was connected to the global ocean during the time of deposition of these shales.

Depleted mantle Nd model ages (T_{DM}) of the black shales and their various components increase with increasing Sm/Nd ratios (Fig. 6). For whole rock shales and their components with Sm/Nd ratios higher than 0.12, which is the upper limit for normal shales (Taylor and McLennan, 1985; McLennan, 1989), T_{DM} ages are anomalously high and variable. Previous studies have identified high $^{147}\text{Sm}/^{144}\text{Nd}$ and anomalously old T_{DM} as evidence for diagenetic alteration in black shales (Bock et al., 1994; Lev et al., 1999). However, for the Utica black shale samples with Sm/Nd ratios similar to normal shales, shown by the shaded area in Fig. 6, the depleted mantle Nd model ages range from 1.6 to 2.3 Ga (average 1.9 Ga), indicating their derivation from pre-Grenvillian age sources, possibly from Laurentian basement rocks. These data are in contrast with the findings of a previous study (Anderson and Samson, 1995) that suggested the influence of a juvenile source for these

Taconic basin sediments. This contrasting observation, however, requires further investigation.

6. Conclusions

- (1) Isolated components of black shales, such as organic, carbonate and sulfide fractions, as well as the whole rocks show overlapping but characteristically different Nd-isotopic compositions. If the present day Nd-isotopic composition of black shales is affected by diagenesis (thermal maturation), which alters the Sm/Nd ratio of the rock, it can be argued that the different components of black shales are affected to different degrees for a given diagenetic process or different diagenetic processes affect the different components. Alternatively, the variation in Nd-isotopic compositions of the shale components could also reflect differences in provenance, especially for the immature shales. Our Nd-isotopic data indicate multiple sources of sediments for the Taconic Foreland Basin, which hosts the Utica shales.
- (2) Although thermal maturation of black shales mobilize all LREE, mobility of La relative to Sm is greater in the mature shales compared to the post mature shales, which show greater mobility of Nd relative to Sm.
- (3) Nd isotopic composition of black shales, especially mature and post mature shales and their components are controlled by thermal maturation of these rocks while those of the immature shales reflect source heterogeneity.
- (4) The initial Nd isotopic composition at 420 Ma of the black shales, showing no diagenetic imprint with Sm/Nd ratios similar to average shales, overlap with the global seawater Nd-isotopic composition at that time. This observation suggests that the Taconic Foreland Basin, which hosts the Utica Shale Magnafacies, was connected to the global ocean during the time of deposition of these shales.
- (5) Depleted mantle Nd model ages of the Utica black shales and their various components increase with increasing Sm/Nd ratios. However, for the samples showing no diagenetic imprint, the depleted mantle Nd model ages range from 1.6 to 2.3 Ga (average 1.9 Ga). This age indicates that sediments in the Taconic basin, especially the black shales of the Utica shale Magnafacies, were derived from pre-Grenvillean age sources. This conclusion may need further investigation as it is in contrast to some previous studies that suggested the influence of a juvenile source for these Taconic basin sediments.

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