



Association of uranium with macerals in marine black shales: Insights from the Upper Devonian New Albany Shale, Illinois Basin

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ABSTRACT

Marine organic-rich shales generally have high uranium content associated with sedimentary organic matter. However, organic matter in black shales is not homogeneous, but instead a mixture of different macerals. The uranium content and organic petrographic composition of 27 New Albany Shale samples indicate differential contributions of macerals to the uranium content in the Upper Devonian New Albany Shale of the Illinois Basin. Specifically, uranium is mainly associated with amorphous organic matter (microbially degraded phytoplankton, zooplankton, and bacterial biomass), where an average uranium content of approximately 550 ppm has been estimated. The amorphous organic matter's lack of structure, as well as admixed with mineral grains ($< 7.8 \mu\text{m}$) suggest that it originated via microbial degradation in surficial sediments. Uranium may have been incorporated into amorphous organic matter during phytoplankton degradation and amorphous kerogen formation early in diagenesis. Pore-water redox conditions and pH control the reduction of uranium (VI) and its incorporation into amorphous organic matter. Alginite derived from *Tasmanites* algae (average uranium content < 10 ppm) contributes minimally to uranium content. Terrestrial organic matter in the New Albany Shale contains on average ~ 20 ppm uranium, and because it accounts for $< 10\%$ of total organic matter in the New Albany Shale, its contribution is equally negligible.

1. Introduction

Organic matter quantity, quality, and thermal maturity fundamentally control the hydrocarbon generation potential of source rocks (Tissot and Welte, 1984; Peters and Cassa, 1994), and can be of marine as well as terrestrial origin (Potter et al., 1998; Flores and Suárez-Ruiz, 2017; Mastalerz et al., 2018). Alginite, amorphous organic matter, vitrinite, and inertinite are common macerals in black shale successions (Mastalerz et al., 2018), and their origin (Stach et al., 1982; ICCP, 1998; Taylor et al., 1998; Paction et al., 2011; Kus et al., 2016, 2017; Pickel et al., 2017), chemical structure (Chen et al., 2012; Dutta et al., 2013; Wei et al., 2016; Hackley et al., 2017; Liu et al., 2019a), hydrocarbon generation potential (Revill et al., 1994; Petersen, 2006; Vigran et al., 2008), thermal maturation (Burnham and Sweeney, 1989; Huang, 1996; Hackley and Cardott, 2016; Hackley et al., 2017; Liu et al., 2019a), and petrographic characteristics (Stach et al., 1982; ICCP, 1998; Taylor et al., 1998; Kus et al., 2017; Liu et al., 2017; Pickel et al., 2017; Hackley et al., 2018; Liu et al., 2019a) have been studied extensively.

Gamma radiation in marine black shales is largely due to uranium (U), with lesser contributions from potassium and thorium (Rider, 2002). U content in marine black shales typically ranges from 15 to 60 ppm (Fertl and Chilingar, 1988), but some black shales are characterized by much higher values, such as the Cambrian Alum Shale in Sweden, which contains about 100 to 300 ppm U and is Europe's largest low-grade source of U (Andersson et al., 1983; Lecomte et al., 2017; Yang et al., 2018, 2019). It is a common assumption that most of the U in marine black shales was sourced from soluble U in ancient sea water (Swanson, 1960, 1961; Anderson et al., 1989; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991).

Uranium in marine black shales (type II kerogen sequence) is typically associated with organic matter, but may in addition be incorporated into sedimentary phosphate (Swanson, 1960, 1961). Because of the common covariation of U and organic matter content, gamma-ray logs can be used to estimate total organic carbon (TOC) content in marine black shales (Swanson, 1960, 1961; Leventhal, 1981; Schmoker, 1981; Fertl and Chilingar, 1988; Bohacs and Schwalbach, 1994; Lüning and Kolonic, 2003; Passey et al., 2010; Sondergeld et al.,

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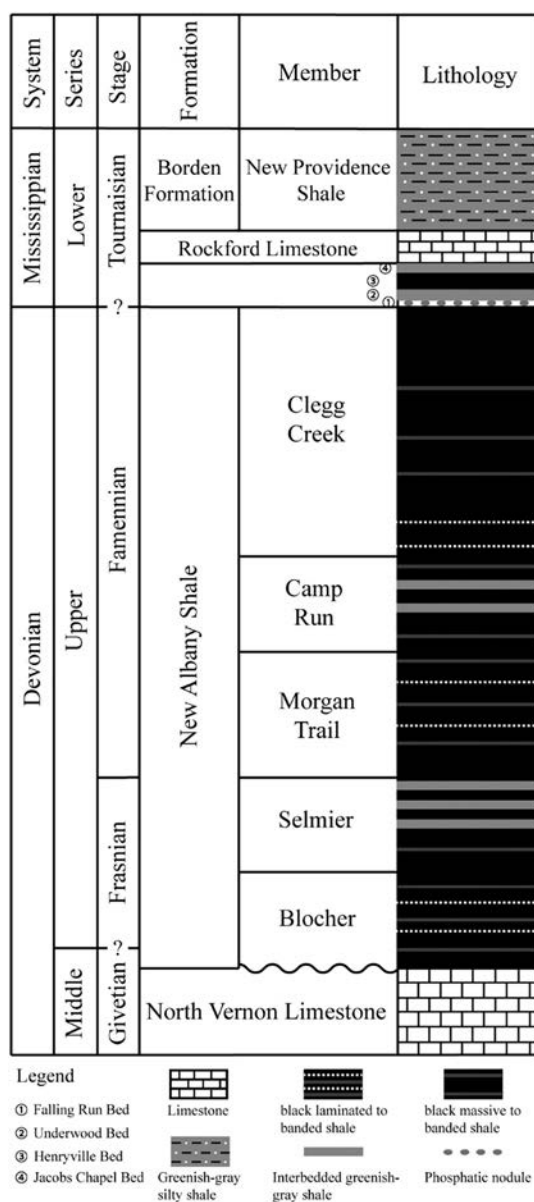


Fig. 1. Generalized stratigraphy of the New Albany Shale, Illinois Basin. Modified from Lineback (1964, 1968); Lazar (2007).

2010; Liu et al., 2019b). However, some marine black shales have high TOC yet low U content (Lüning and Kolonic, 2003), suggesting that in the absence of U-bearing minerals, different types of organic matter may have distinctly different U contents. To our knowledge, there are no studies where the association of U with specific macerals has been examined.

The overall goal of this investigation is to study the heterogeneity of organic matter in the New Albany Shale and examine the association of U with organic matter and specific macerals (alginite, amorphous organic matter, terrestrial organic matter). Our study provides a new perspective on U accumulation in marine black shales.

2. Geological setting

The New Albany Shale was deposited in the Illinois Basin, an epicontinental sea, during the late Devonian (Lineback, 1964, 1968; Beier and Hayes, 1989). Geographically, it extends from central and southern Illinois to southwestern Indiana and western Kentucky. Stratigraphically, the New Albany Shale overlies the Middle Devonian North

Vernon Limestone and is unconformably overlain by the Falling Run Bed (Fig. 1; Lineback, 1964, 1968; Schieber and Lazar, 2004; Lazar, 2007). It is composed of the Blocher, Selmier, Morgan Trail, Camp Run, and Clegg Creek Members in ascending order (Fig. 1; Lineback, 1964, 1968). These members consist largely of black to brownish laminated to banded shales and greenish-gray bioturbated shales (common in the Selmier and Camp Run Members) (Fig. 1; Lineback, 1964, 1968; Schieber and Lazar, 2004; Lazar, 2007; Liu et al., 2019b).

The thermal maturity of the New Albany Shale ranges from vitrinite reflectance (R_o) 0.5% at the margin of the Illinois Basin to R_o 1.5% in the Hicks Dome area of Hardin County, Illinois (Strapoć et al., 2010; Mastalerz et al., 2013). TOC contents range from < 1% to 20 wt% (Chou et al., 1991), with an average TOC content of 6–7 wt% (Lazar, 2007; Liu et al., 2019b). Organic matter in the New Albany Shale is classified as type II kerogen (Chou et al., 1991; Akar et al., 2015) and has high hydrocarbon generation potential. In early mature New Albany Shale, the organic matter is dominated by oil-prone liptinite macerals such as amorphous organic matter and alginite, with lesser and variable contents of terrestrial organic matter including vitrinite and inertinite (Mastalerz et al., 2012, 2013; Liu et al., 2017, 2019a, 2019b). Thermally mature New Albany Shale is dominated by solid bitumen derived from oil-prone macerals (Mastalerz et al., 2013; Liu et al., 2017, 2019a).

3. Materials and analytical methods

3.1. Samples

A complete New Albany Shale drill core 1–3 Kavanaugh from Daviess County, Indiana, USA (Schieber and Lazar, 2004; Lazar, 2007; Liu et al., 2019b) and an outcrop of the New Albany Shale in Shepherdsville, Kentucky, USA (Fig. 2) were selected to study the heterogeneity of organic matter in the New Albany Shale. The core is at the early-maturity stage (R_o 0.55%; Liu et al., 2019b), suggesting that organic matter in this core was not significantly altered by thermal maturation. The U contents of 44 previously analyzed New Albany Shale samples (Lazar, 2007) and organic petrographic compositions of 33 New Albany Shale samples (Liu et al., 2019b) from the studied New Albany Shale core were used in combination to examine the association of U with organic matter and specific macerals. Within this data set, 27 samples have U content, TOC content, and organic petrographic composition data (Table 1). Samples of ~2 cm thickness were cut from the drill core for geochemical and organic petrographic analyses. Sample depths are shown in Table 1.

A thin coal layer (compressed tree limb, about 1 mm thick) embedded within the New Albany Shale was collected from the Shepherdsville outcrop (Fig. 3). The coal sample was sealed immediately with Ziplock bags to prevent contamination. Because the coal layer occurs within the matrix of marine black shales, it affords a unique opportunity to examine the differences in U content between terrestrial and marine organic matter in the New Albany Shale.

3.2. Organic petrography

Shale samples were crushed to rock chips of < 1 mm and made into whole-rock pellets. The pellets were polished and R_o values of vitrinite (50 measurements per sample) were determined with a Zeiss Photoscope III microscope. The organic petrographic characteristics of macerals were documented using a reflected-light microscope (Leica DM2500 P) and oil immersion. The organic petrographic compositions of shale samples were determined via point counting (500 points, organic matter only). Correlative microscopy (reflected-light and scanning electron microscopy) was used to study the occurrence and texture of amorphous organic matter and alginite via imaging with a field-emission scanning electron microscope (SEM) (FEI Quanta 400 FEG), following the methods of correlative microscopy in Liu et al. (2017).

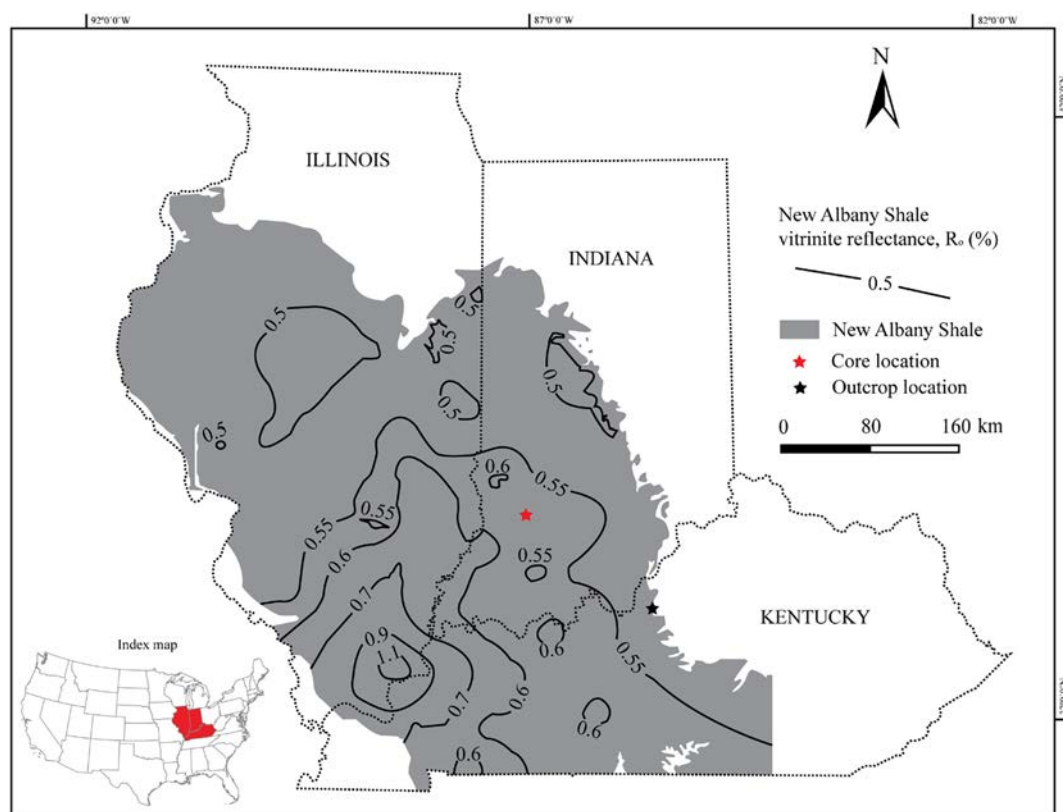


Fig. 2. Map showing the locations of the core and outcrop and the extent of the New Albany Shale in the Illinois Basin. Modified from Mastalerz et al. (2013).

Table 1

Depth (m), uranium (U), phosphorus (P), total sulfur (S), total organic carbon (TOC) content, and organic petrographic composition of 27 New Albany Shale samples from drill core 1–3 Kavanaugh.

Member	Sample	Depth (m)	U (ppm)	P (%)	S (%)	TOC (wt%)	Organic petrographic composition (volume %, on mineral-matter-free basis)					
							AOM	Alginite	Liptodetrinite	Vitrinite	Inertinite	SB
Clegg Creek	NAS-1	610.50	58.45	0.04	2.83	14.87	44.3	40.0	2.5	1.1	8.2	3.9
	NAS-2	612.66	51.25	0.03	4.70	9.54	64.8	21.9	1.4	1.6	5.3	5.0
	NAS-3	613.94	57.35	0.05	4.28	9.57	53.5	38.4	2.7	1.0	1.5	2.9
	NAS-4	615.54	63.88	0.04	4.82	11.93	67.9	20.6	1.3	2.3	2.1	5.8
	NAS-5	616.46	56.72	0.04	4.53	10.81	59.5	32.5	2.1	1.0	1.1	3.8
	NAS-6	617.44	33.27	0.07	3.52	8.05	48.7	44.5	2.9	0.4	1.0	2.5
	NAS-7	619.00	13.12	0.03	0.93	1.11	57.5	34.8	2.1	1.3	1.0	3.3
	NAS-8	620.25	16.62	0.34	4.66	9.98	19.3	74.0	3.8	0.4	1.2	1.3
Camp Run	NAS-9	621.87	13.94	0.02	1.44	2.48	40.6	51.7	2.7	1.1	1.1	2.8
	NAS-10	623.82	19.59	0.04	2.31	4.91	57.0	35.8	2.0	0.6	0.9	3.7
	NAS-11	624.64	14.87	0.03	2.14	4.74	68.4	25.3	1.7	0.8	0.8	3.0
	NAS-12	626.12	18.34	0.03	2.30	5.01	58.5	34.8	2.2	0.6	0.8	3.1
	NAS-13	628.54	23.65	0.02	2.10	4.98	73.5	18.3	1.3	0.6	0.7	5.6
	NAS-14	629.99	24.49	0.03	1.60	7.29	54.3	36.8	2.6	0.9	1.1	4.3
	NAS-15	630.73	14.90	0.03	3.19	16.29	11.0	83.1	4.1	0.2	0.2	1.4
	NAS-16	631.58	21.92	0.03	2.74	5.94	48.1	44.0	2.7	0.6	0.8	3.8
Morgan Trail	NAS-18	632.94	30.07	0.02	2.45	8.57	42.2	48.6	2.8	0.9	1.3	4.2
	NAS-19	633.70	34.95	0.02	4.19	8.09	26.0	67.4	3.4	0.4	0.7	2.1
Selmier	NAS-20	635.26	13.35	0.03	3.29	5.65	9.6	82.7	5.4	0.4	0.4	1.5
	NAS-21	636.86	6.79	0.03	3.19	3.61	21.0	71.0	3.9	0.7	1.2	2.2
	NAS-22	638.32	13.62	0.03	1.51	1.92	10.9	80.3	5.2	0.7	1.0	1.9
	NAS-23	639.36	23.10	0.03	1.85	5.32	22.0	71.0	4.1	0.4	0.6	1.9
	NAS-25	640.64	35.02	0.04	3.48	8.62	21.6	69.6	4.2	0.7	1.5	2.4
Blocher	NAS-26	641.49	10.00	0.09	1.53	5.91	16.0	70.8	4.7	0.9	4.2	3.4
	NAS-30	645.84	10.97	0.03	1.90	6.54	72.9	14.7	1.9	0.8	1.1	8.6
	NAS-31	646.97	15.31	0.03	1.87	8.37	70.0	15.1	2.4	0.8	3.7	8.0
	NAS-32	648.30	17.73	0.04	1.71	9.87	68.6	15.8	2.1	1.0	4.7	7.8
	Average		26.42	0.05	2.78	7.41	44.7	46.1	2.9	0.8	1.8	3.7

U, P, S, and TOC content data are from Lazar (2007). Sample number, depth, and organic petrographic composition data are from Liu et al. (2019b). AOM = amorphous organic matter; SB = solid bitumen.

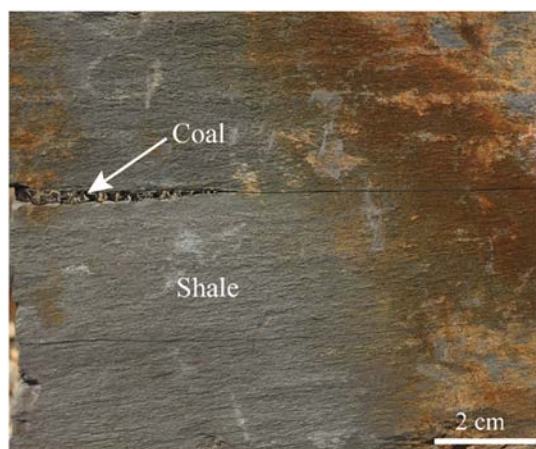


Fig. 3. Thin coal layer embedded within the New Albany Shale from Shepherdsville, Kentucky, USA.

3.3. Geochemical analysis

The U content of the thin coal layer collected from the Shepherdsville outcrop was measured with inductively coupled plasma-mass spectrometry (X series II ICP-MS) in pulse counting mode. The details of sample processing by microwave digestion and ICP-MS analysis are described in Dai et al. (2011).

4. Results

4.1. Organic petrographic characteristics

Core and outcrop both show R_o values of 0.55%, and are therefore of the same thermal maturity. The primary organic matter constituents are mainly amorphous organic matter, alginite, liptodetrinite, vitrinite, and inertinite, with amorphous organic matter and alginite being dominant (Table 1; Liu et al., 2019b). Amorphous organic matter refers to structureless organic matter, often admixed with the matrix minerals of organic-rich shales. It is derived from microbially degraded phytoplankton, zooplankton, and bacterial biomass (Teichmüller, 1989; Taylor et al., 1998; Pacton et al., 2011; Kus et al., 2017). Under a reflected-light microscope, amorphous organic matter occurs as organic streaks parallel to bedding, with inclusions of clay minerals and other clay-sized and silt-sized mineral grains (Fig. 4).

Alginite is another major contributor to organic matter in the New Albany Shale and is mainly derived from the cysts of *Tasmanites* algae. *Tasmanites*, named after a well-known occurrence in the Tasmanite oil shale of Tasmania, Australia (Revill et al., 1994), are the fossil remains

of unicellular green algae that belong to the class Prasinophyceae (Tappan, 1980; Vigran et al., 2008; Dutta et al., 2013) and are very common in Devonian black shales in North America (Schieber, 1996; Schieber et al., 2000; Liu et al., 2017, 2019a, 2019b). Alginite derived from *Tasmanites* algae is characterized by long, unbranched alkyl chains (Lin and Ritz, 1993; Mastalerz et al., 2012; Dutta et al., 2013; Hackley et al., 2017) and has very high hydrocarbon generation potential (Revill et al., 1994; Vigran et al., 2008).

In immature to early mature samples, *Tasmanites* cysts are brown-amber-colored in reflected white light and oil immersion and show greenish-yellow fluorescence under blue light irradiation (Fig. 5). Most of the *Tasmanites* cysts measure between 200 and 300 μm in length and are flattened by compaction, although in places they may be filled with early diagenetic pyrite and quartz (Schieber, 1996; Schieber et al., 2000).

The coal sample is composed entirely of collotelinite with a mean R_o of 0.51%, which is 0.04 lower than the R_o of surrounding shales. The collotelinite is homogenous with poorly preserved cellular structure in places (Fig. 6A) and does not show fluorescence under blue light irradiation. Small vitrinite particles ($\sim 5 \mu\text{m}$) in the coal sample are very similar to those observed in adjacent shale samples (Fig. 6), suggesting that the small vitrinite particles in shales are detrital vitrinite.

4.2. Uranium content

Based on 44 analyses (Lazar, 2007), U contents in the New Albany Shale range from 6.79 to 63.88 ppm, with an average value of 24.20 ppm. U content does not correlate ($R^2 = 0.001$) with P content (Fig. 7A), but has a positive correlation ($R^2 = 0.53$) with TOC content (Fig. 7B). U-bearing minerals such as uraninite, coffinite, and monazite, were not identified under the SEM coupled with energy dispersive spectroscopy. It therefore appears that organic matter, rather than inorganic phases, is associated with U in the New Albany Shale. Judging from the U versus TOC relationship (Fig. 7B) and assuming that organic matter has a TOC content of 76.4% (Durand and Monin, 1980), the U content in bulk organic matter of the New Albany Shale is approximately 260 ppm. The intercept at 2.79 ppm (Fig. 7B) could be considered the U content associated with detrital materials, assuming that all authigenic U is associated with organic matter. If one estimates the detrital U content in the New Albany Shale on the basis of an average thorium (Th) content of 10.94 ppm (Lazar, 2007) and an assumed detrital end member U/Th ratio of 0.24 (Wedepohl, 1995), one arrives at a value of approximately 2.66 ppm, very close to the observed intercept at 2.79 ppm (Fig. 7B).

Twenty-seven New Albany Shale samples that were analyzed for both U content and maceral quantities (Lazar, 2007; Liu et al., 2019b) show that a broad positive trend ($R^2 = 0.48$) exists between U content and the amorphous organic matter fraction (Table 1; Fig. 8A) and that U

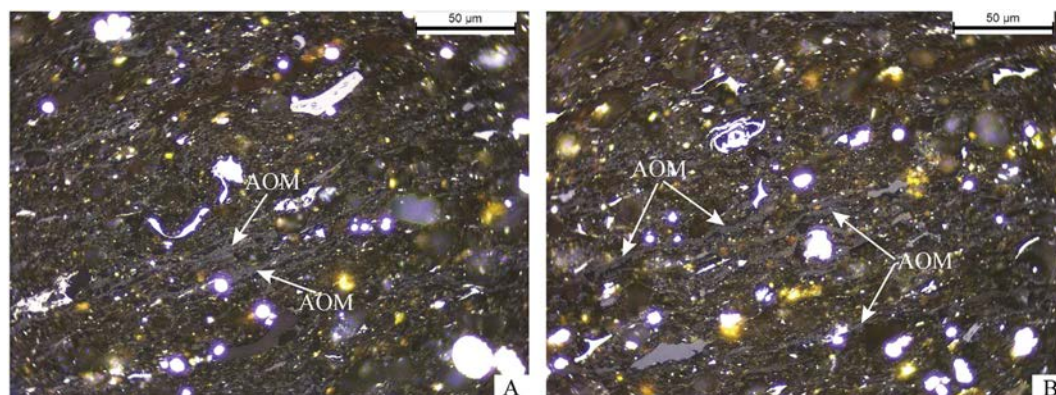


Fig. 4. Photomicrographs of amorphous organic matter in reflected white light and oil immersion. Note the structureless texture of amorphous organic matter. AOM = amorphous organic matter.

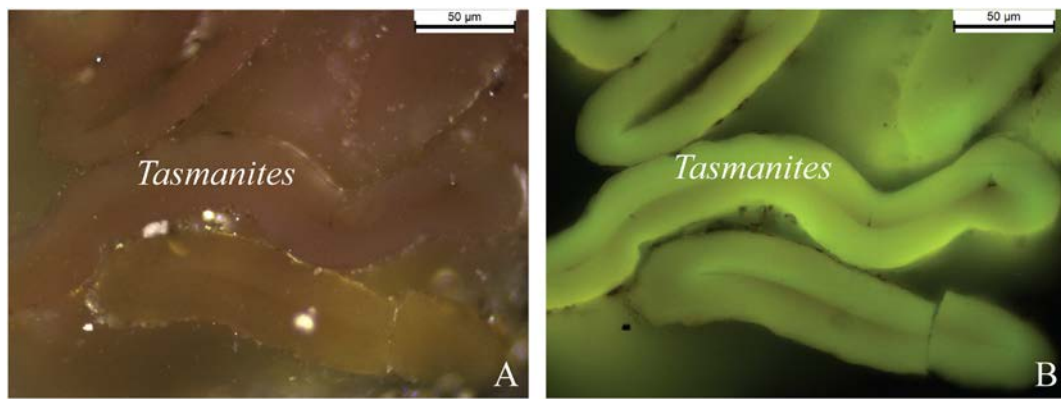


Fig. 5. Photomicrographs of compacted *Tasmanites* cysts in reflected white light and oil immersion (A) and in fluorescence mode (B).

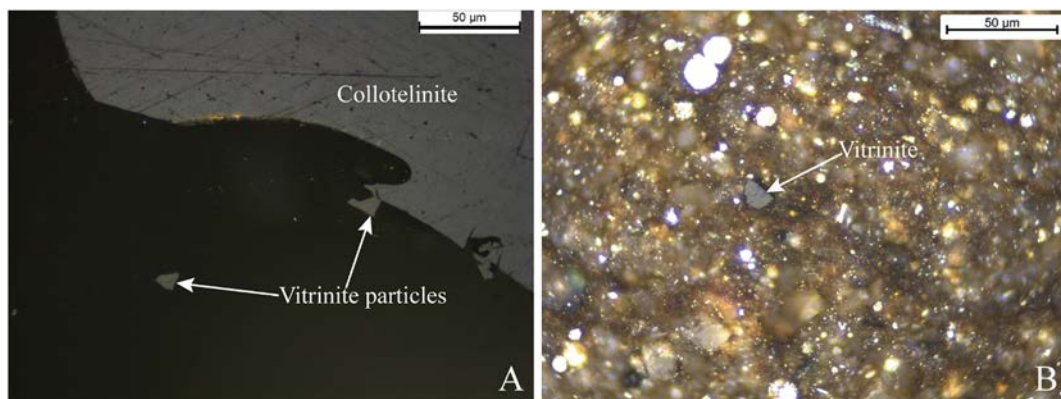


Fig. 6. Photomicrographs of vitrinite in the coal sample and shales that surround the coal layer in reflected white light and oil immersion. (A) Vitrinite in the coal sample. (B) Small dispersed vitrinite particles in adjacent shale samples. Note that the shape and size of small dispersed vitrinite particles in panel B are very similar to those in adjacent coal sample in panel A, suggesting the same origin.

has no apparent correlation ($R^2 = 0.01$) with the alginite fraction (Table 1; Fig. 8B), indicating that U associated with organic matter is largely contained in amorphous organic matter. Sample NAS-15 serves to illustrate these interrelationships. It has a TOC content of 16.29%, but its U content is only 14.9 ppm (Table 1), because organic matter in this sample is strongly dominated by alginite (83.1%) derived from *Tasmanites* cysts (Table 1). Interestingly, three samples from the basal Blocher Member show high TOC and amorphous organic matter content

and low U content. After these three samples were removed, the coefficient of determination between U content and amorphous organic matter fraction reached 0.80 (Fig. 8C). The reasons for the mismatch between U and amorphous organic matter content in the Blocher Member will be discussed in section 5. According to the relationship between U and amorphous organic matter content (Fig. 8C), U content in amorphous organic matter is about 550 ppm, assuming a 76.4% TOC content of amorphous organic matter (Durand and Monin, 1980). There

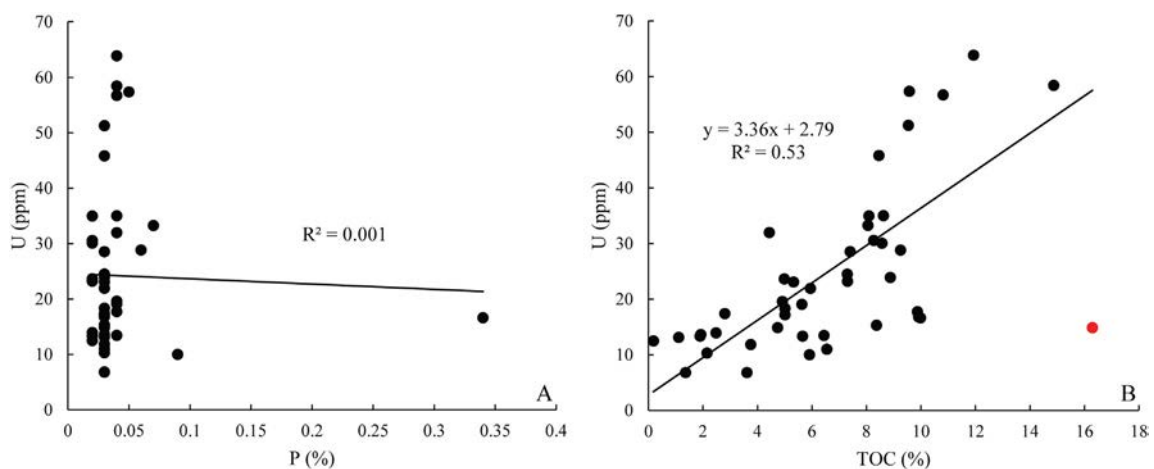


Fig. 7. Cross-plots of uranium content versus phosphorus (A) and total organic carbon content (B) based on 44 New Albany Shale samples. The outlier sample NAS-15 (Table 1; highlighted in red) has a U content of 14.9 ppm and TOC content of 16.29%, respectively, and is not included to derive the relationship between U and TOC content in panel B. U, P, and TOC content data are from Lazar (2007). TOC = total organic carbon; P = phosphorus; U = uranium. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

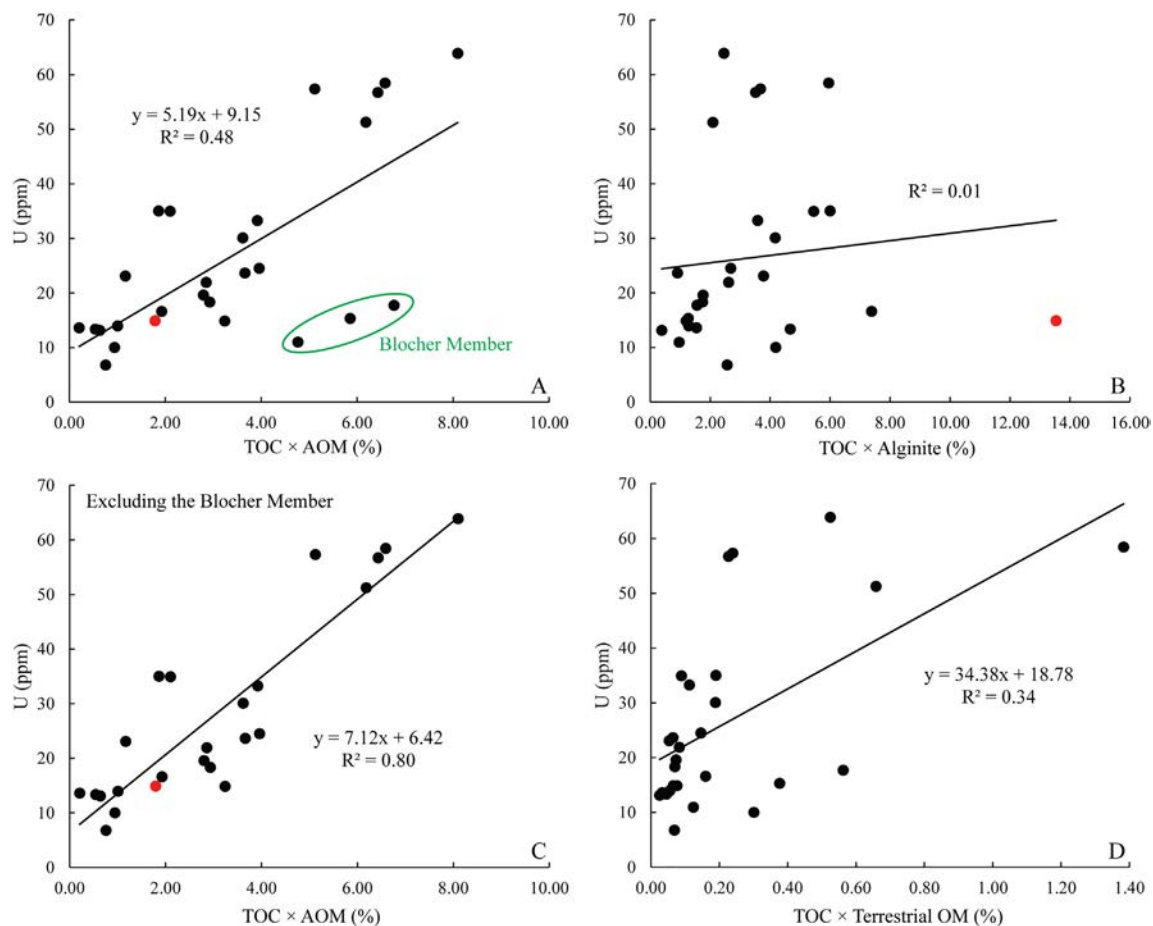


Fig. 8. Correlations between uranium content and composition of organic matter based on 27 New Albany Shale samples. Panel C excludes the three samples from the Blocher Member (circled in green in panel A). The sample highlighted in red refers to sample NAS-15 (Table 1), which has a 14.9 ppm U content and 16.29% TOC content. U content data are from Lazar (2007). Organic petrographic composition data are from Liu et al. (2019b). TOC = total organic carbon; AOM = amorphous organic matter; U = uranium. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is an appearance of a slight positive correlation between U content and the terrestrial organic matter fraction (Fig. 8D). However, given the low U content of the analyzed coal layer (19.56 ppm), this correlation is probably not significant.

5. Discussion

U in marine organic-rich shales is generally associated with organic matter (Swanson, 1960, 1961; Lüning and Kolonic, 2003; Liu et al., 2019b), phosphate (biogenic and diagenetic; Swanson, 1960, 1961; Parnell, 1984), and aragonite (Tatsumoto and Goldberg, 1959; Kitano and Oomori, 1971; Amiel et al., 1973; Gothmann et al., 2019). In particular, the association of U with organic matter has been reported by many studies (Swanson, 1960, 1961; Leventhal, 1981; Fertl and Chilingar, 1988; Bohacs and Schwalbach, 1994; Lüning and Kolonic, 2003; Liu et al., 2019b). However, some black shales with high TOC contents show low concentrations of U (Lüning and Kolonic, 2003), probably a manifestation of the heterogeneity of sedimentary organic matter in organic-rich shales. How different macerals contribute to U content in the New Albany Shale is one of the key aspects of our study (Fig. 8).

Amorphous organic matter is the main host of U in the New Albany Shale (Fig. 8A, C). It is commonly admixed with clay minerals and clay-sized and very fine silt-sized (< 7.8 µm) mineral grains, which, together with its amorphous texture, suggests that it underwent microbial degradation in surface sediments (Fig. 9). Fishman et al. (2012) and Hackley et al. (2018) reported the incorporation of fine-grained mineral

matrix within lamellar bituminite (a synonym of amorphous organic matter). Milliken et al. (2014) also reported inclusions of silt- and clay-sized mineral grains within immature amorphous kerogen in modern eastern Mediterranean sapropels. In the New Albany Shale, bottom current reworking and bedload transport of accumulating and eroded seafloor muds is indicated by fine parallel to low-angle downlapping laminae (Schieber et al., 2007; Schieber, 2011; Schieber, 2016), and it seems plausible therefore that mixing of degrading organic matter and mineral grains occurred as a consequence of these processes. In contrast, alginite derived from *Tasmanites* algal bodies has a smooth surface and does not show any microbial degradation (Fig. 10).

Hexavalent U (VI) is generally soluble in seawater, but will be reduced to the less soluble tetravalent U (IV) under reducing conditions (Langmuir, 1978; Anderson et al., 1989; Klinkhammer and Palmer, 1991). Some researchers have posited that U is precipitated and adsorbed by sedimentary organic matter as disseminated uranium dioxide (UO₂) or incorporated into organic matter as urano-organic complexes during organic matter decomposition (Breger and Schopf, 1955; Swanson, 1960, 1961; Cumberland et al., 2016). Because amorphous organic matter is derived from organic matter more labile than *Tasmanites* cysts (Schieber, 2001), microbial degradation of amorphous organic matter probably consumed dissolved oxygen in pore water and promoted reducing conditions favorable for the reduction of U (VI). It is thus possible that U was incorporated into amorphous organic matter during phytoplankton degradation and amorphous kerogen formation near the sediment-water interface (Fig. 11).

Three samples (NAS-30, 31, 32; Table 1) from the Blocher Member

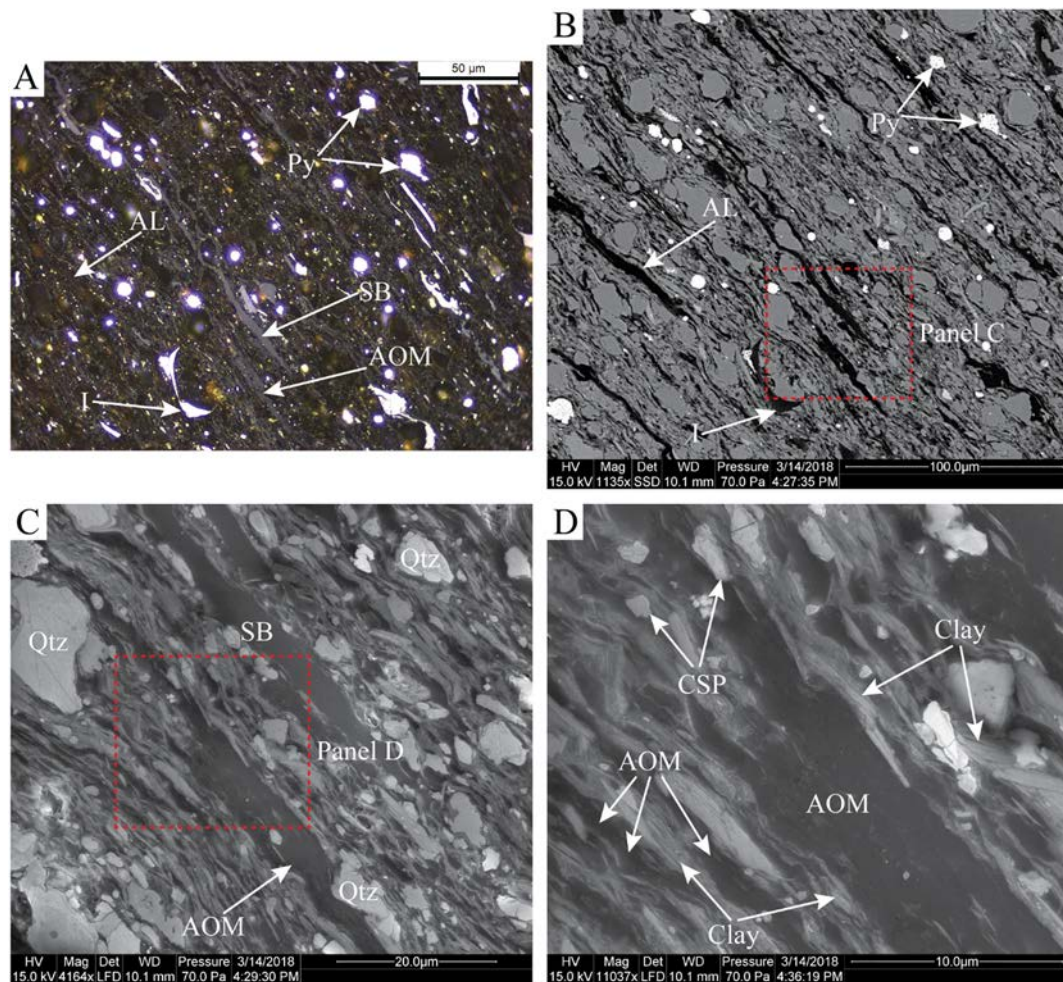


Fig. 9. Photomicrographs of amorphous organic matter in the New Albany Shale in reflected white light and oil immersion (A) and its correlative SEM images (B, backscattered electron image; C – D, secondary electron images). Panel B is the same view as panel A under SEM. Note the mixed nature of amorphous organic matter with clay minerals and clay-sized particles. AOM = amorphous organic matter; AL = algalite; SB = solid bitumen; I = inertinite; Py = pyrite; Qtz = quartz; CSP = clay-sized particle.

have high TOC and amorphous organic matter content, but contain low U content (Table 1; Fig. 8A). Soluble U (VI) can only be reduced to less soluble U (IV) under reducing conditions (Langmuir, 1978; Anderson et al., 1989; Klinkhammer and Palmer, 1991). However, bottom water was likely oxic to dysoxic during deposition of the Blocher Member (Lazar, 2007; Ocubalidet et al., 2018), an unfavorable setting for the reduction of U and its incorporation into amorphous organic matter. Liu et al. (2019b) also suggested that variably oxygenated bottom waters during the Blocher Member deposition due to water column mixing by storms and waves resulted in low U contents and consequently low gamma-ray intensities. Therefore, although amorphous organic matter is overall the primary contributor to U content in the New Albany Shale, only amorphous organic matter formed under reducing conditions has high U content.

The reducing environment required for the reduction of U (VI) can be either local or wide ranging. Pyrite is very common in the Blocher Member, suggesting that locally reducing conditions existed in the sediments during deposition of the Blocher Member, even though the depositional environment (the overlying bottom water) was generally oxic to dysoxic (Lazar, 2007; Ocubalidet et al., 2018; Liu et al., 2019b). U can potentially be adsorbed or complexed by amorphous organic matter under locally reducing condition. However, when locally reducing conditions were disrupted by reworking of bottom sediments, reduced U could plausibly have diffused out of the sediments into the overlying bottom water (Shaw et al., 1994; Morford and Emerson,

1999). Total sulfur (mostly pyritic sulfur; Frost, 1996) content in the Blocher Member is lower than other members (Table 1; Lazar, 2007), suggesting that pore water was less sulfidic during early diagenesis of sediments in the Blocher Member. Because the reduction and precipitation of U(VI) involves the action of hydrogen sulfide (Swanson, 1961), reduction of U(VI) is less efficient in the Blocher Member. In comparison, the Clegg Creek Member has the highest total sulfur content (Table 1) and the most oxygen-deficient condition during deposition (Lazar, 2007; Ocubalidet et al., 2018; Liu et al., 2019b), which is favorable for U reduction and enrichment. As a result, U content in the Clegg Creek Member is the highest in the New Albany Shale (Table 1). The incorporation of U into amorphous organic matter, therefore, requires reducing environments with less disruption.

Aside of potential control via pore-water redox conditions, the pore-water pH may also influence the enrichment of U in marine black shales. The Blocher Member is characterized by a high carbonate content (Frost and Shaffer, 1994; Liu et al., 2020), which suggests more alkaline conditions during its deposition compared to other members of the New Albany Shale. The U(VI) adsorption capacity of bituminous shales and clay minerals and precipitation of U-bearing substances decreases with increasing pH from pH ~ 6–7 (normal bottom water pH; Swanson, 1961) to alkaline conditions (Swanson, 1961; Khouya et al., 2010; Bachmaf and Merkel, 2011; Ortaboy and Atun, 2014). With decreased U(VI) adsorption, there would also be less U(VI) available for reduction. Above scenario is supported by prior studies where an inverse

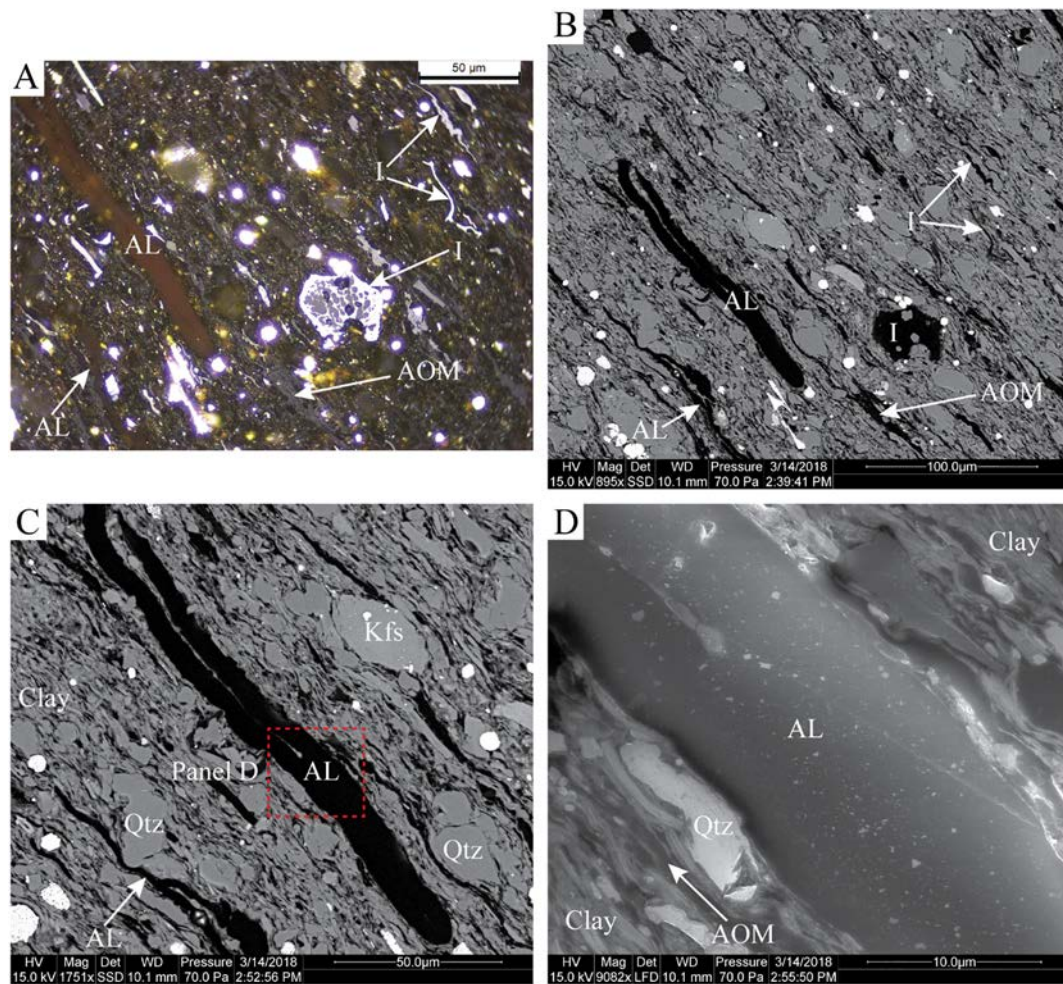


Fig. 10. Photomicrographs of alginite in the New Albany Shale in reflected white light and oil immersion (A) and its correlative SEM images (B – C, backscattered electron images; D, secondary electron image). Panel A is the same view as panel B under a reflected-light microscope. Note the distinct algal bodies of *Tasmanites* cysts. AL = alginite; AOM = amorphous organic matter; I = inertinite; Qtz = quartz; Kfs = K-feldspar.

relationship exists between U and carbonate contents of marine black shales (McKelvey and Nelson, 1950; Swanson, 1961). Thus, pore-water redox conditions as well as pH appear to influence the incorporation of U into amorphous organic matter as examined in this study and marine carbonaceous shales in general.

Alginite appears to contribute minimally to U content (Fig. 8B),

otherwise sample NAS-15 (Table 1), having a TOC content of 16.29 wt % and organic matter being dominated by alginite (83.1% of total organic matter), should have a much higher U content. Previously, Leventhal (1981) measured U content in hand-picked *Tasmanites* cysts collected from the New Albany Shale in Bullitt County, Kentucky and found that *Tasmanites* cysts contain < 10 ppm U, which is much lower

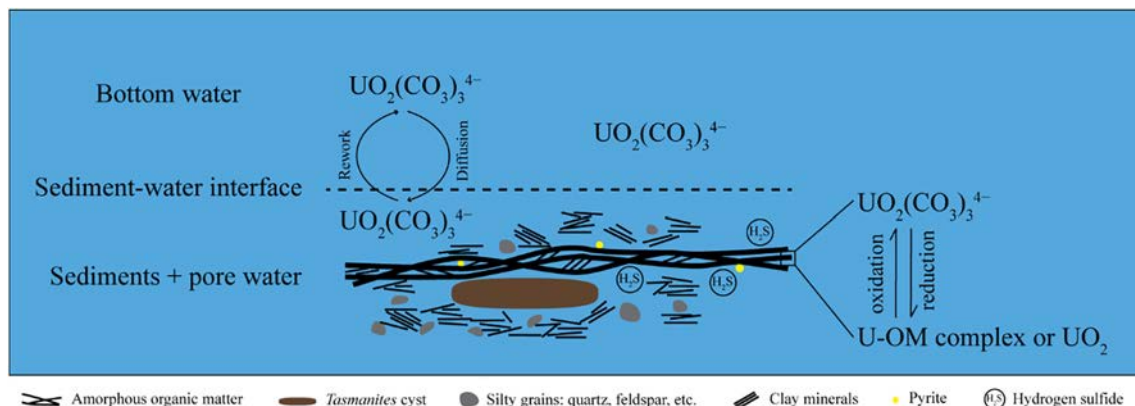


Fig. 11. Schematic drawing of the enrichment process of U in marine black shales during early diagenesis. U (VI) was soluble in bottom water and pore water above and below sediments-water interface, respectively. U (VI) get adsorbed onto amorphous organic matter and then get reduced to urano-organic complex or uraninite under locally reducing conditions in the presence of H_2S . When sediments get reworked, insoluble reduced U (IV) could be oxidized to soluble U (VI) in oxygenated pore water.

than the estimated U content in amorphous organic matter (550 ppm). Miyake et al. (1970) reported that the U contents in modern marine plankton and algae are 0.17–0.78 and 0.04–2.35 ppm, respectively, which supports the assumption that water column organisms in the ocean do not have high U contents and that U is likely incorporated into amorphous organic matter during early diagenesis. Therefore, U associated with organic matter is likely a diagenetic product sourced from the dissolved U (VI) that diffused from bottom water into the pore space of underlying sediments (Anderson et al., 1989; Klinkhammer and Palmer, 1991). Consequently, telalginite with a distinct appearance of algal bodies does not significantly contribute to U content of black shales such as the New Albany Shale. However, when partially or completely degraded, marine algae transform to lamellar alginite or amorphous organic matter (Teichmüller, 1989; Taylor et al., 1998; Paction et al., 2011; Kus et al., 2017) that may contain large and variable concentrations of U.

The average U content in coals worldwide is about 2.4 ppm (Ketris and Yudovich, 2009), suggesting that typical terrestrial organic matter does not have high concentrations of U, although U associates with organic matter in some U-rich coals (Dai et al., 2008, 2015a, 2015b; Seregin and Finkelman, 2008). In the latter case, however, U was not derived from coal-forming plants, but instead sourced from U-bearing solutions under certain geological conditions. For example, Dai et al. (2015b) reported that U in the high-U Yili coals from the Yili Basin (China) came from U-bearing solutions in the overlying sandstones during the epigenetic stage. Microporous inertinite provided channels for migration of U-bearing solutions and U-bearing minerals such as uraninite and coffinite precipitated in cellular pores of inertinite (Dai et al., 2015b). The average U concentration in Indiana coals is about 1.77 ppm (Mastalerz and Drobnik, 2007), an indication that terrestrial organic matter in the Illinois Basin should have low U contents. Nonetheless, terrestrial organic matter in marine organic-rich shales can have higher U contents than observed in coals. For example, Breger and Schopf (1955) reported that coal bands in the Chattanooga Shale and Cleveland Shale (time-equivalent with the New Albany Shale) contain 330 and 85 ppm of U, respectively. They proposed that the precursor woody materials absorbed U during the formation of organo-uranium compounds while degrading in marine environments.

In this study, the measured U content of a thin coal band embedded within the New Albany Shale is 19.56 ppm, which is higher than the average U content in Indiana coals, but significantly lower than the estimated U content of bulk organic matter (260 ppm) in the New Albany Shale. In addition, because terrestrial organic matter accounts for < 10% of total organic matter in the New Albany Shale (Table 1; Liu et al., 2019a, 2019b), the contribution of terrestrial organic matter to U content in the New Albany Shale is considered negligible.

Amorphous organic matter is the dominant oil-prone liptinite maceral in marine black shales (Mastalerz et al., 2018). It will transform to hydrocarbons and solid bitumen (as defined through organic petrography) during thermal maturation and does not occur in its original form at high maturities (Hackley and Cardott, 2016; Liu et al., 2019a). If U was originally associated with amorphous organic matter at low thermal maturity, it is our assumption that with increasing maturity (late oil and gas windows) U should associate with amorphous organic matter-derived solid bitumen or pyrobitumen. However, it should be noted that it is impossible to distinguish amorphous organic matter-derived solid bitumen from alginite-derived solid bitumen at high maturities.

The association of U with solid bitumen or pyrobitumen has been extensively investigated in the study of U ore deposits (e.g., Parnell, 1988, 1994; Mossman and Nagy, 1996; Mossman et al., 2005; Mossman, 1999; Fuchs et al., 2016, 2017), where U-bearing solutions and hydrocarbon fluids played a main role in U enrichment. The geologic setting of these studies, and that of our study, where the focus is on sedimentological and early diagenetic controls on U enrichment (Fig. 11), is fundamentally different. In this study, U was sourced from

ancient sea water, and not from U-bearing solutions underground. Because shales generally have very low permeability, late diagenetic introduction of U via U-bearing solutions and hydrocarbon fluids does not appear to be a viable process for U enrichment observed in the New Albany Shale. In fine-grained sediments, the highest porosity and permeability are present early in depositional history, and U diffusing in from overlying seawater during early diagenesis therefore appears to be the most plausible scenario for the observed U enrichment. Hydrocarbon generation from kerogen had not yet started at that point, and therefore hydrocarbon fluids or bitumen were not relevant to U enrichment observed in this study.

6. Conclusions

Uranium in the New Albany Shale mainly associate with organic matter. Varying macerals contributed differently to the U content. Amorphous organic matter with an average U content of approximately 550 ppm is the primary host phase. Alginite derived from *Tasmanites* cysts (average U content < 10 ppm) contributes negligible U. Terrestrial organic matter generally contains rather small amounts of U (average U content ~ 20 ppm) and due to its low abundance in these shales contributes little to the overall U content in the New Albany Shale. Because primary organisms in the oceans do not have high U contents, U was likely incorporated into amorphous organic matter during phytoplankton degradation and amorphous kerogen formation during early diagenesis when pore-water redox conditions and pH influenced the reduction of U (VI) and its incorporation into amorphous organic matter. In situations where macerals other than amorphous organic matter are significant or dominant components of the organic matter in a black shale, gamma-ray logs are most likely a poor proxy for TOC content.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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