

Methods

All samples were ground to < 200 mesh size with a ceramic mortar and pestle, acidified with a 1 N HCl solution to remove carbonates, washed to neutrality, and dried at 50° C. The carbonate-free residues were weighed into tin capsules and converted to CO₂ and N₂ for isotope analysis using a Carlo Erba elemental analyzer (EA) coupled to an Optima stable isotope ratio mass spectrometer (Micromass, Manchester, UK). Carbon and nitrogen isotope compositions were determined on gases from a single combustion using a dual furnace system composed of an oxidation furnace at 1020°C and a reduction furnace at 650°C. Sulfur isotope compositions were determined on gases using a single oxidation/reduction furnace at 1030°C. The resulting gases were chemically dried and directly injected into the source of the mass spectrometer. Isotope results are reported in per mil (‰) notation as follows:

$$\delta^X E = [R_{\text{sample}}/R_{\text{standard}} - 1] 1000 (\text{‰})$$

where X is the heavy isotope of the element E and R is the abundance ratio of the heavy to light isotopes (¹³C/¹²C, ¹⁵N/¹⁴N or ³⁴S/³²S) of that element. The standard for carbon is the Peedee Belemnite limestone (PDB), for nitrogen the standard is atmospheric N₂ (Air) and for sulfur the standard is Canyon Diablo Troilite (CDT). Standards are assigned δ^XE values of 0.0‰. For sulfur and carbon the value is corrected for the mass overlap with the isotopes of oxygen. The reproducibility of the measurement is typically better than ±0.2‰ for these elements using the continuous flow interface on the Optima. In the laboratory, the samples are commonly measured against tanks of carbon dioxide, nitrogen, and sulfur dioxide gases that have been calibrated against NBS 22, atmospheric N₂ and NBS 127, respectively. Reproducibility between duplicate standards for %C_{org}, %N_{total}, and %S_{total} averaged ± 2% of the abundance.

Total phosphorus (TP) was determined using the combustion method (Aspila et al. 1976). A 0.5 g aliquot of each sample was combusted at 550°C for two hours, allowed to cool, and shaken overnight in a water bath in a 1 N HCl solution. The P content of the decanted solution was determined spectrophotometrically. The reproducibility for replicate samples and standards was ± 3.5% of the measured abundance.

The total sulfur content of samples was determined using a Carlo Erba elemental analyzer (EA). All sulfur was assumed to be in the form of reduced sulfides, primarily pyrite. The degree of pyritization (DOP) was determined by the ratio

$$\text{DOP} = \text{Fe}_{\text{pyr}}/(\text{Fe}_{\text{pyr}} + \text{Fe}_x)$$

where Fe_x represents the weight percent reactive iron and Fe_{pyr} represents the weight percent of pyrite-bound Fe (Raiswell et al. 1988). Pyrite-bound Fe was determined from the total pyrite-bound S based on the 1:2 stoichiometry of FeS₂ (weight percent S × 0.871). Reactive Fe was determined by washing 0.1 g of sample in 5 ml of 1N HCl for

24 hours (Leventhal & Taylor 1990). A 10 µl aliquot of supernatant was mixed with 4 ml of FerroZine reagent and the Fe concentration was determined spectrophotometrically at a wavelength of 562 nm.

References

Aspila, K.I., Agemian, H. & Chau, A.S.Y., 1976, A Semi-automated Method for the Determination of Inorganic, Organic and Total Phosphate in Sediments, *Analyst*, 101, pp. 187-97.

Leventhal, J. & Taylor, C., 1990, Comparison Of Methods To Determine Degree Of Pyritization, *Geochimica et Cosmochimica Acta*, 54(9), pp. 2621-5.

Over, D.J., 2002, The Frasnian/Famennian boundary in central and eastern United States, *Palaeogeography Palaeoclimatology Palaeoecology*, 181(1-3), pp. 153-69.

Raiswell, R., Buckley, F., Berner, R.A. & Anderson, T.F., 1988, Degree Of Pyritization Of Iron As A Paleoenvironmental Indicator Of Bottom-Water Oxygenation, *Journal of Sedimentary Petrology*, 58(5), pp. 812-9.

Supplemental Figure Captions

Figure DR1. Stratigraphy of the Upper Kellwasser (UKw) interval at three sites in the Hanover Shale Member of the Java Formation of western New York. The top of the UKw interval marks the Frasnian/Famennian boundary, defined by the appearance of the Famennian conodont *Palmatolepis triangularis* (Over 2002). At all three sites the interval consists of laminated black shales, with the exception of a silty layer at Irish Gulf, bounded by bioturbated gray/green shales.

Figure DR2. Crossplot of normalized section thickness and mean total phosphorus (TP) abundance versus relative offshore distance. The thickness of the UKw interval diminishes exponentially with increasing distance from the shoreline and the clastic sediment source. As a terrestrial mineral weathering product, the flux of P also declines in an exponential manner.

Figure DR1

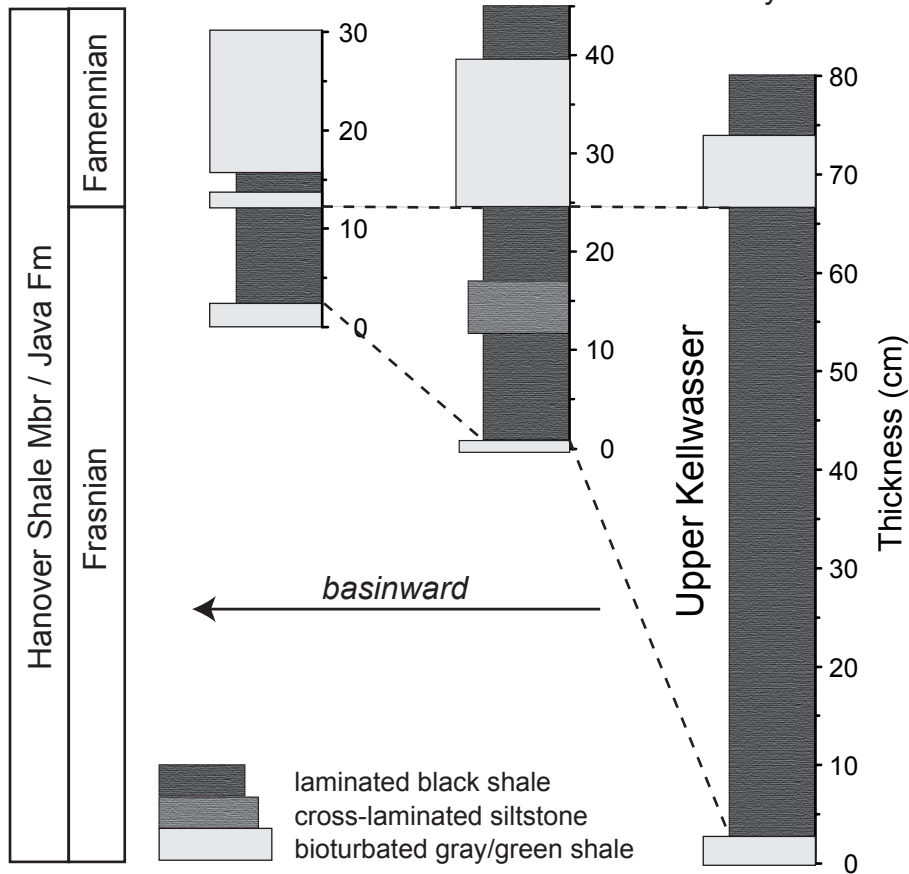


Figure DR2

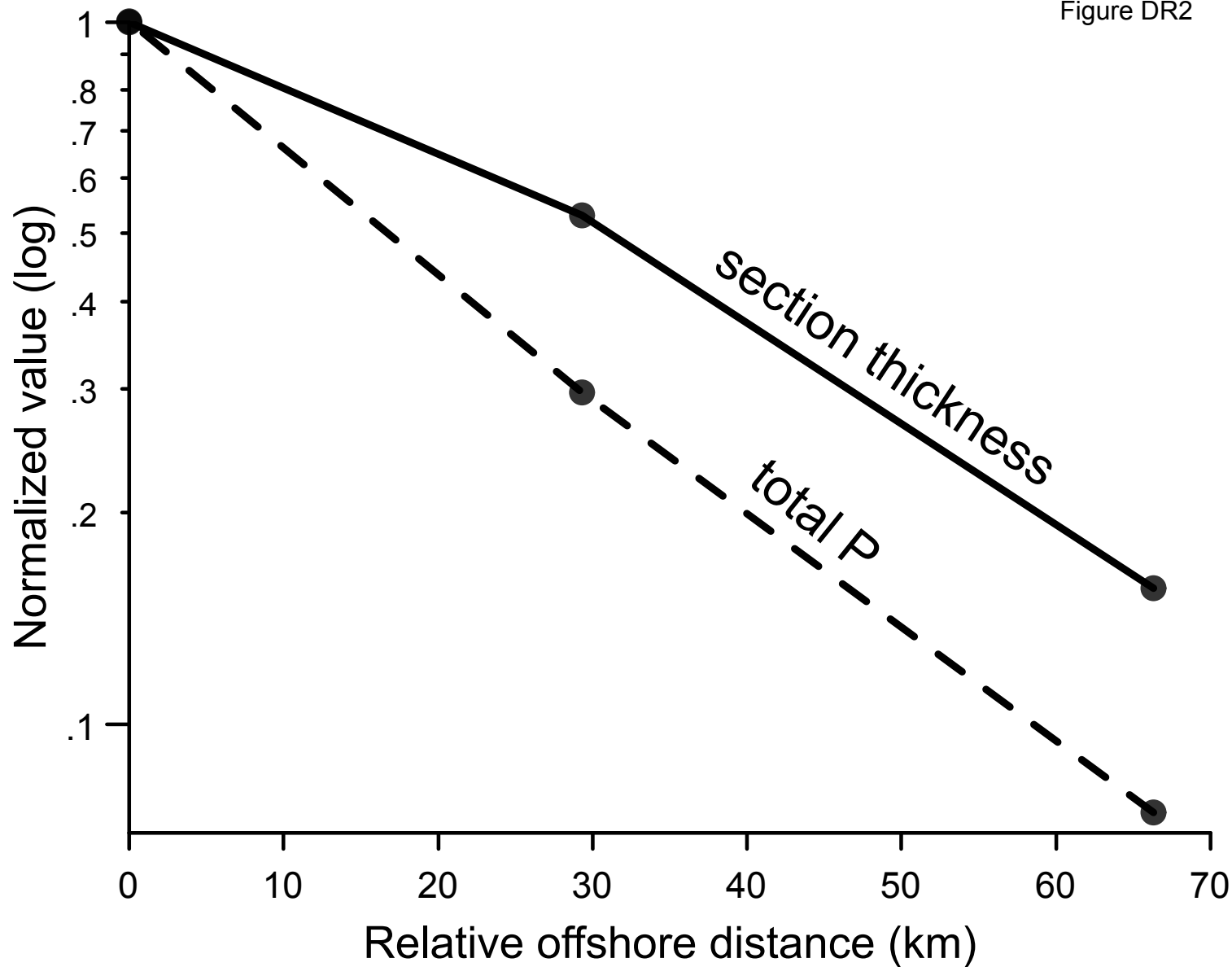


Table DR1

Perry Farm											
Sample	Thickness (cm)	TOC	TN	TP	$\delta^{15}\text{Corg}$	$\delta^{15}\text{Ntotal}$	$\delta^{34}\text{Sbulk}$	TOC/TN	TOC/TP	DOP	
								(molar)	(mol)		
PF01	1.5	0.83	0.09	0.038	-28	1.8	-24.7	11	56	0.75	
PF02	4.5	1.49	0.11	0.038	-29	0.6	-25.9	16.1	102	0.74	Ukw
PF03	7.5	1.96	0.11	n/d	-28.5	-0.1	-27.1	20.6	n/d	n/d	Ukw
PF04	16	2.71	0.14	0.04	-28.9	-0.3	-25.8	23.1	176	0.76	Ukw
PF05	18.5	2.49	0.12	0.04	-28.4	-0.6	-25.1	24.6	159	0.79	Ukw
PF06	21	2.52	n/d	0.042	-28.8	-0.1	-24.6		156	0.78	Ukw
PF07	23	1.96	0.1	0.049	-29.8	0.2	-24.4	23.1	104	0.78	Ukw
PF08	25	2.4	0.13	0.039	-28.8	-0.1	-24.5	21.2	158	0.79	Ukw
PF09	27	2.32	0.12	0.038	-28.7	-0.7	-25	22.5	159	0.79	Ukw
PF10	29	2.73	0.13	0.039	-28.7	-0.6	-24.4	24.5	181	0.79	Ukw
PF11	31	2.44	0.13	0.041	-28.5	-0.4	-22.8	22	155	0.79	Ukw
PF12	33	2.42	0.13	0.036	-28.7	-0.4	-24.2	21.7	172	0.79	Ukw
PF13	35	2.72	0.13	0.041	-28.6	-0.7	-24	24.8	172	0.81	Ukw
PF14	37	3.02	0.14	0.043	-28.5	-0.8	-24.6	26.1	179	0.8	Ukw
PF15	41	2.41	0.12	0.054	-27.8	-0.9	-26.3	24.2	115	0.8	Ukw
PF16	43	2.64	0.13	0.056	-27.8	-0.8	-23.9	24.2	121	0.83	Ukw
PF17	45	3.73	0.15	0.051	-26.7	-0.2	-23.9	28.3	188	0.78	Ukw
PF18	47	3.46	0.18	0.055	-27.2	0.1	-23.9	22.8	162	0.83	Ukw
PF19	49.5	3.04	0.15	0.051	-25.7	0	-17.8	23.9	153	0.85	Ukw
PF20	52.5	2.63	0.13	0.052	-26.2	-0.2	-19.7	23.1	132	0.84	Ukw
PF21	55	2.17	0.12	0.045	-25.7	1.3	-18.4	20.9	125	0.81	Ukw
PF22	59	1.94	0.11	0.046	-25.6	-0.1	-21.9	20.8	109	0.85	Ukw
PF23	61	2.35	0.11	0.044	-26	-0.1	-27.5	25	137	0.79	Ukw
PF24	63	2.82	0.14	0.04	-26.4	-0.6	-27.3	24.4	182	0.79	Ukw
PF25	65	2.51	n/d	0.041	-26.4	0.2	-27.6	n/d	159	0.83	Ukw
PF26	68.5	0.39	0.07	0.044	-23.8	1.1	-25.7	6.8	23	0.78	

Irish Gulf											
Sample	Height (cm)	TOC	TN	TP	d13Corg	d15Ntotal	d34Sbulk	TOC/TN	TOC/TP	DOP	
								(molar)	(molar)		
IG03	0	0.39	0.09	0.026	-28.9	0.3	-28.1	5.1	38	0.69	
IG05	1.5	3.84	0.15	0.031	-29.1	-0.6	-21.9	29.5	321	0.8	Ukw
IG06	3.5	2.2	0.12	0.033	-29.3	-0.1	-29.5	20.9	173	0.77	Ukw
IG07	5.5	2.79	0.14	0.034	-29.6	-0.3	-29.7	22.6	213	0.8	Ukw
IG08	7.5	3.51	0.17	0.035	-29.4	0.2	-24.9	24.7	261	0.75	Ukw
IG09	9.5	3.56	0.16	0.037	-29.8	-0.6	-27.1	25.8	250	0.81	Ukw
IG10	11.5	1.18	0.09	0.037	-28.7	0	-19.8	15.8	83	0.71	Ukw
IG11	13.5	1.38	0.09	0.036	-28.5	0.3	-25.3	17.6	99	0.69	Ukw
IG12	15.5	1.66	0.11	0.036	-28.5	0.5	-23.5	17	120	0.7	Ukw
IG13	21.5	3.17	0.16	0.037	-29.3	-0.3	-25.5	23.7	222	0.79	Ukw
IG14	27.5	0.3	0.11	0.034	-23.9	1	-23.2	3.3	23	0.4	

Walnut Creek											
Sample	Height (cm)	TOC	TN	TP	d13Corg	d15Ntotal	d34Sbulk	TOC/TN	TOC/TP	DOP	
								(molar)	(molar)		
WC2	0	0.73	0.13	0.038	-27.5	0.8	-14.7	6.6	50	0.77	
WC3	2	4.06	0.18	0.023	-28.6	-0.3	-16.6	25.9	448	0.85	Ukw
WC4	4	4.28	0.18	0.02	-28.1	0	-21.5	27.3	542	0.82	Ukw
WC5	6	5.16	0.22	0.021	-28.4	-0.4	-23.7	28	626	0.84	Ukw
WC6	8	4.99	0.2	0.023	-28.6	0	-21.8	28.7	568	0.88	Ukw
WC7	10	4.38	0.19	0.021	-28.2	0.1	-7.2	27.1	544	0.89	Ukw
WC8	11.5	0.44	0.13	0.064	-26.9	0.9	-30.2	3.8	18	0.68	