Geological Magazine

A global reference for black shale geochemistry and the T-OAE revisited: Upper Pliensbachian – middle Toarcian (Lower Jurassic) chemostratigraphy in the Cleveland Basin, England

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Supplementary Material

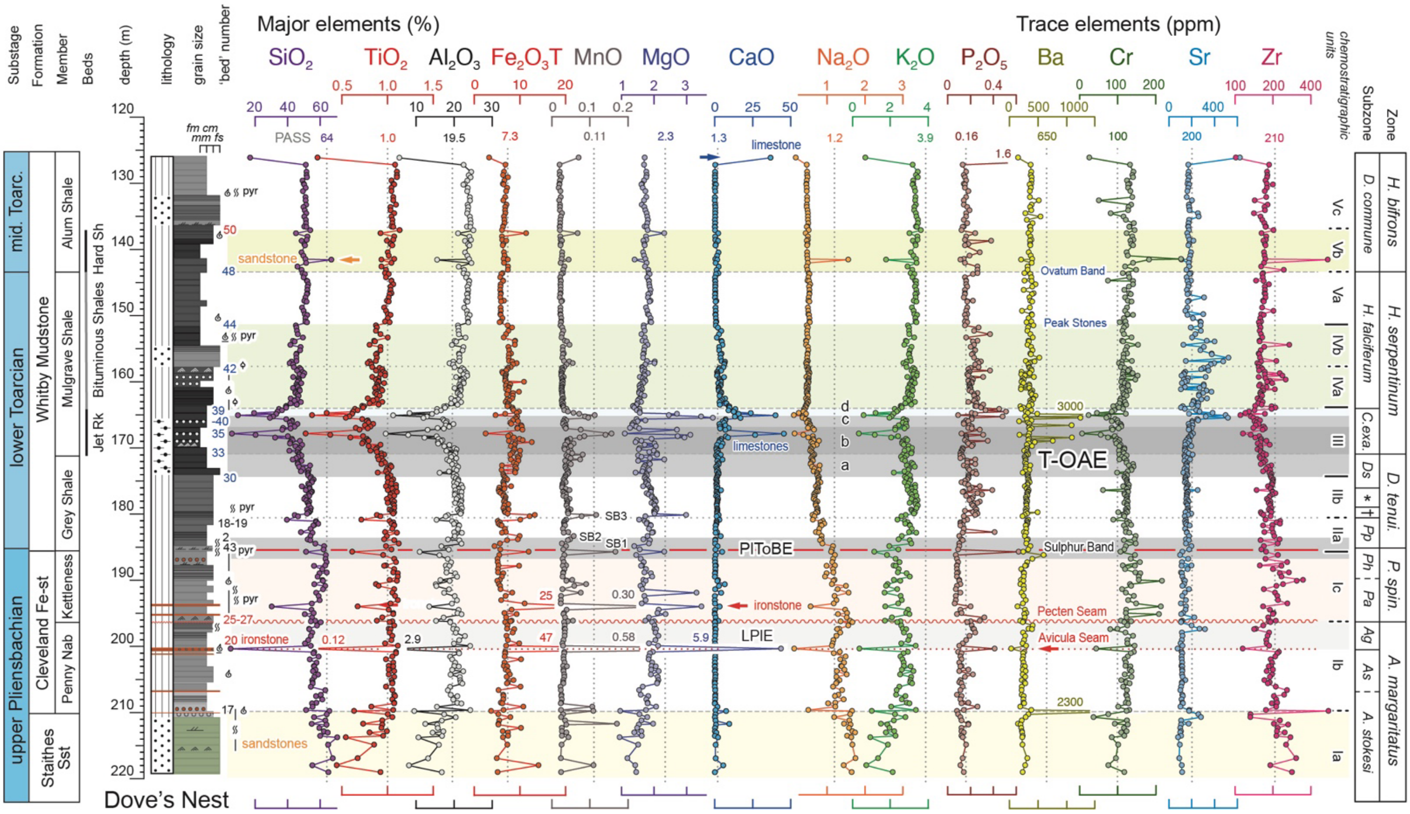

Fig. S1. Geochemical profiles for major elements and selected trace elements through the upper Pliensbachian – middle Toarcian of the Dove's Nest core. 'Bed' numbers, names and biostratigraphy are derived from chemostratigraphic correlation to Hawsker Bottoms for the Pliensbachian (Howarth, 1955), and a Whitby composite section for the Toarcian (Howarth, 1962, 1973, 1992): red, sideritic beds; blue, limestones; black other beds (see Fig. 2). Vertical dotted lines and numbers are reference values for Post-Archean Average Shale (PASS; = average mud of Taylor & McLennan, 2001). Prominent limestone 'bed' 35 (Whale Stones) and 'beds' 39 – 40 (Top Jet Dogger and Millstones), are clearly expressed by their high CaO contents and coincident excursions in most other constituents. Significant shifts in the elemental profiles, combined with coincident changes in $\delta^{13}C_{org}$ and TOC (Fig. 2), are used to define the chemostratigraphic units (see text), modified from the scheme of Remírez & Algeo (2020). Note the similarity of profiles for elements (Si, Ti, Al, K, Cr, Zr) associated principally with the detrital fraction (quartz, clay minerals, heavy minerals). Total Fe expressed as Fe_2O_3*. LPIE = Late Pliensbachian Event; other abbreviations as Figure 2.

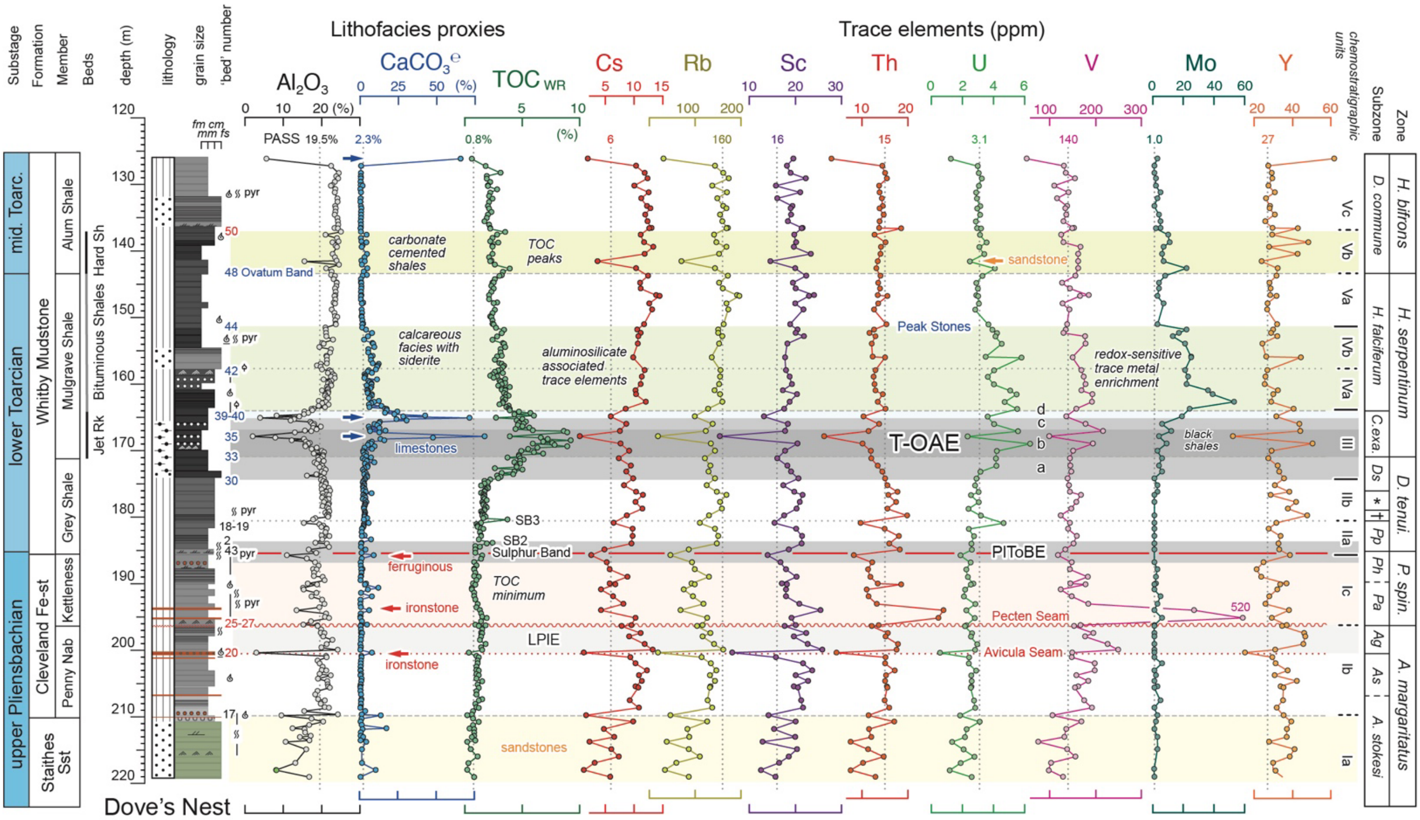

Fig. S2. Geochemical profiles for lithofacies proxies Al_2O_3 (aluminosilicates, principally clay minerals), $CaCO_3^e$ (carbonates; calcite, siderite) and TOC_{WR} (organic fraction) through the upper Pliensbachian – middle Toarcian of the Dove's Nest core, with selected trace elements. Stratigraphy, plotting conventions and abbreviations as in Figure S1. Note the similar profiles for Al_2O_3, Cs, Rb, Sc, Th indicating a close association to the aluminosilicate fraction. Redox-sensitive trace metals U, V and Mo show very different individual distributions but are characteristically enriched in the mid-lower Toarcian, within and above the T-OAE interval. $CaCO_3^e$ calculated from Ca values with the assumption that all Ca occurs in carbonate. TOC_{WR} of Avicula Seam ironstone (200.29 m) corrected for siderite.

Table S3. Pearson r correlation coefficients for selected Dove's Nest geochemical data.

Table S3. Pearson r correlation coefficients for selected Dove's Nest geochemical data.

Constituent	Major elements										Trace elements												Organic matter	
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Ba	Cs	Cr	Mo*	Rb	Sc	Sr	Th	U	V	Y	Zr	TOC_{WR}	TOC_{IR}
SiO_2																								
TiO_2	**0.82**																							
Al_2O_3	**0.63**	**0.93**																						
Fe_2O_3	-0.29	-0.35	-0.36																					
MnO	-0.35	-0.61	-0.78	**0.63**																				
MgO	-0.24	-0.17	-0.22	**0.66**	**0.65**																			
CaO	-0.55	-0.83	-0.84	0.07	**0.52**	-0.09																		
Na_2O	**0.78**	0.48	0.18	0.06	0.14	0.12	-0.36																	
K_2O	0.38	**0.80**	**0.94**	-0.41	-0.82	-0.26	-0.78	-0.05																
P_2O_5	-0.52	-0.63	-0.53	0.24	0.39	0.29	**0.52**	-0.39	-0.48															
Ba	0.30	0.15	0.09	-0.54	-0.16	-0.37	-0.04	0.12	0.08	-0.22														
Cs	0.22	**0.68**	**0.87**	-0.33	-0.81	-0.18	-0.73	-0.18	**0.94**	-0.33	-0.08													
Cr	**0.61**	**0.68**	**0.59**	0.02	-0.23	0.03	-0.59	0.43	0.42	-0.52	-0.07	0.33												
Mo*	-0.50	-0.48	-0.30	-0.18	-0.22	-0.44	0.38	-0.55	-0.20	0.10	-0.10	-0.07	-0.43											
Rb	0.26	**0.70**	**0.88**	-0.43	-0.83	-0.26	-0.71	-0.18	**0.97**	-0.42	0.09	**0.97**	0.30	-0.09										
Sc	**0.58**	**0.63**	**0.60**	-0.08	-0.25	0.16	-0.62	0.41	0.46	-0.12	0.01	0.45	0.44	-0.56	0.42									
Sr	-0.36	-0.37	-0.27	-0.21	0.08	-0.01	0.37	-0.43	-0.20	0.42	0.27	-0.15	-0.62	0.21	-0.11	-0.08								
Th	**0.57**	**0.78**	**0.71**	-0.02	-0.31	0.09	-0.75	0.43	**0.61**	-0.56	-0.05	**0.52**	0.69	-0.57	0.49	**0.59**	-0.42							
U	-0.19	-0.01	0.14	-0.48	-0.52	-0.59	-0.01	-0.39	0.34	-0.19	0.26	0.27	-0.37	0.37	0.38	-0.29	0.20	-0.19						
V	-0.06	0.06	-0.02	0.42	0.25	0.47	-0.37	0.30	0.00	-0.29	-0.26	0.01	0.20	-0.29	-0.02	0.19	-0.26	0.41	-0.14					
Y	0.33	0.11	-0.03	0.06	0.23	0.23	-0.05	0.46	-0.14	0.37	0.02	-0.17	0.00	-0.54	-0.23	**0.53**	0.02	0.21	-0.32	0.00				
Zr	**0.67**	**0.50**	0.27	-0.03	-0.06	-0.13	-0.35	0.69	0.10	-0.65	0.20	-0.05	**0.63**	-0.36	0.01	0.07	-0.68	0.45	-0.18	0.20	-0.05			
TOC_{WR}	-0.73	-0.37	-0.13	0.03	-0.15	-0.03	0.13	-0.77	0.14	0.22	-0.22	0.22	-0.41	0.41	0.24	-0.49	0.16	-0.36	**0.53**	-0.01	-0.48	-0.51		
TOC_{IR}	-0.69	-0.65	-0.55	-0.08	0.19	-0.07	0.49	-0.52	-0.31	0.22	0.12	-0.30	-0.68	0.45	-0.22	-0.68	0.29	-0.64	**0.53**	-0.01	-0.36	-0.35	**0.71**	
$\delta^{13}C_{org}$	0.42	0.44	0.33	0.20	0.05	0.41	-0.41	0.53	0.18	-0.17	-0.19	0.19	0.42	-0.53	0.11	**0.53**	-0.22	**0.62**	-0.55	0.34	0.36	0.30	-0.58	-0.68

Highly significant positive and negative correlations ($r \geq 0.5$) are highlighted in bold and red, respectively. Correlations judged to be statistically not significant (permutation $p \geq 0.01$) are in grey.

Table S4. Loading coefficients for PC1 to PC3 resulting from the principal component analysis (PCA).

Constituent	PC 1 (48.4%)	PC 2 (22.9%)	PC 3 (9.8%)
SiO_2	**0.14**	0.09	**0.22**
TiO_2	**0.16**	-0.01	0.07
Al_2O_3	**0.14**	-0.08	0.01
Fe_2O_3	-0.03	**0.12**	-0.20
MnO	-0.18	**0.40**	-0.20
MgO	0.01	**0.12**	-0.23
CaO	**-0.76**	**0.22**	**0.16**
Na_2O	**0.17**	**0.31**	**0.32**
K_2O	**0.14**	-0.14	-0.05
P_2O_5	-0.15	0.05	-0.29
Ba	0.02	0.01	**0.17**
Cs	**0.19**	-0.24	-0.13
Cr	**0.13**	0.05	0.09
Mo*	-0.34	**-0.61**	**0.42**
Rb	**0.13**	-0.17	-0.07
Sc	0.08	0.03	-0.03
Sr	-0.09	-0.04	-0.11
Th	**0.13**	0.03	-0.01
U	-0.01	-0.12	0.02
V	0.05	0.04	-0.08
Y	0.02	**0.12**	-0.05
Zr	**0.15**	**0.16**	**0.38**
TOC_{WR}	-0.11	**-0.33**	**-0.44**

Percentage of the total variance is indicated for each component. High positive and negative loadings are highlighted in bold black and red, respectively.

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