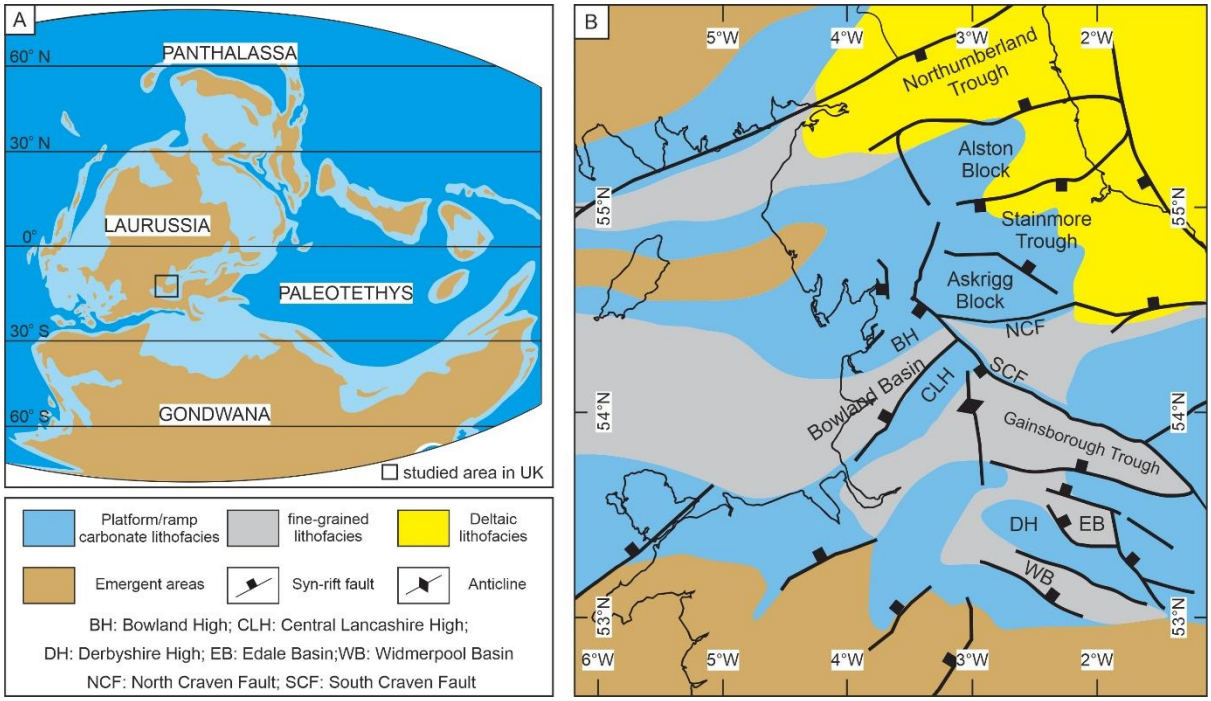

Fig. 1 (A) Mississippian (340 Ma) global paleogeography (modified from Boucot et al., 2013), showing the northern England study area (black rectangle); (B) regional paleogeography of northern England during the Asbian (336- 332 Ma), showing the occurrence of isolated basins surrounded by carbonate platforms and shelves (modified from Cope et al., 1992).

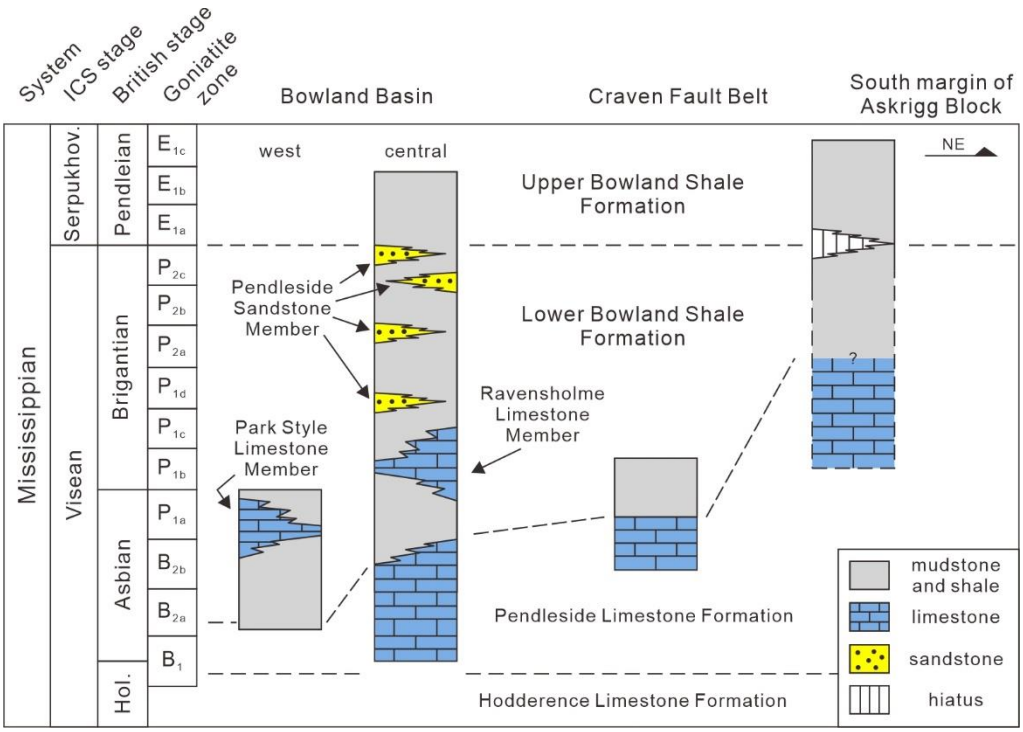

Fig. 2 Summary cross section through the Bowland Basin, Craven Fault Belt; Hol. = Holkerian; Serpukhov. = Serpukhovian; ICS stands for International Commission on Stratigraphy; dashed lines show the formation boundaries (after Earp et al., 1961; Aitkenhead et al., 1992; Waters et al., 2017).

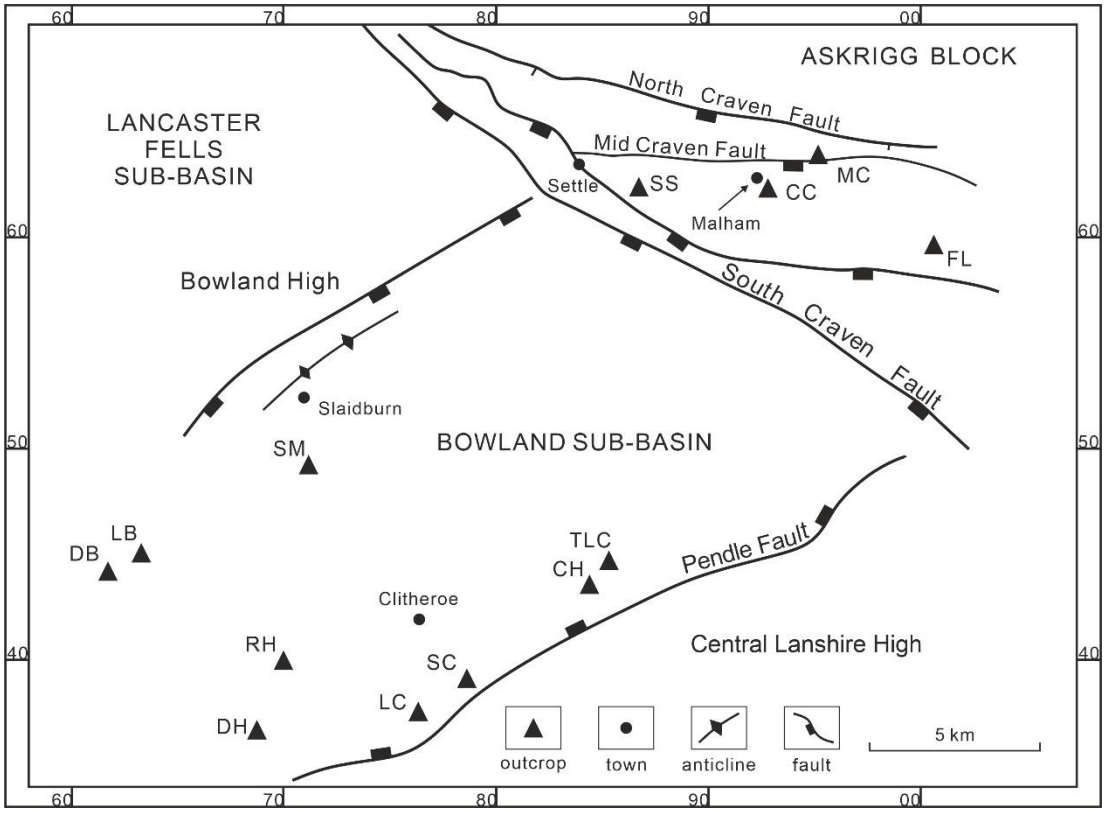

Fig. 3 Study area in the Bowland Basin, Craven Fault Belt, and the southern Askrigg Block. Outcrop locations are Dobson Brook (DB), Leagram Brook (LB), Smelthwaite Farm (SM), School Share (SS), Cow Close (CC), Moor Close Gill (MC), Dinckley Hall (DH), River Hodder (RH), Light Clough (LC), Swarden Clough (SC), Clough Head Beck (CH), Tory Log Clough (TLC), and Fell Lane (FL).

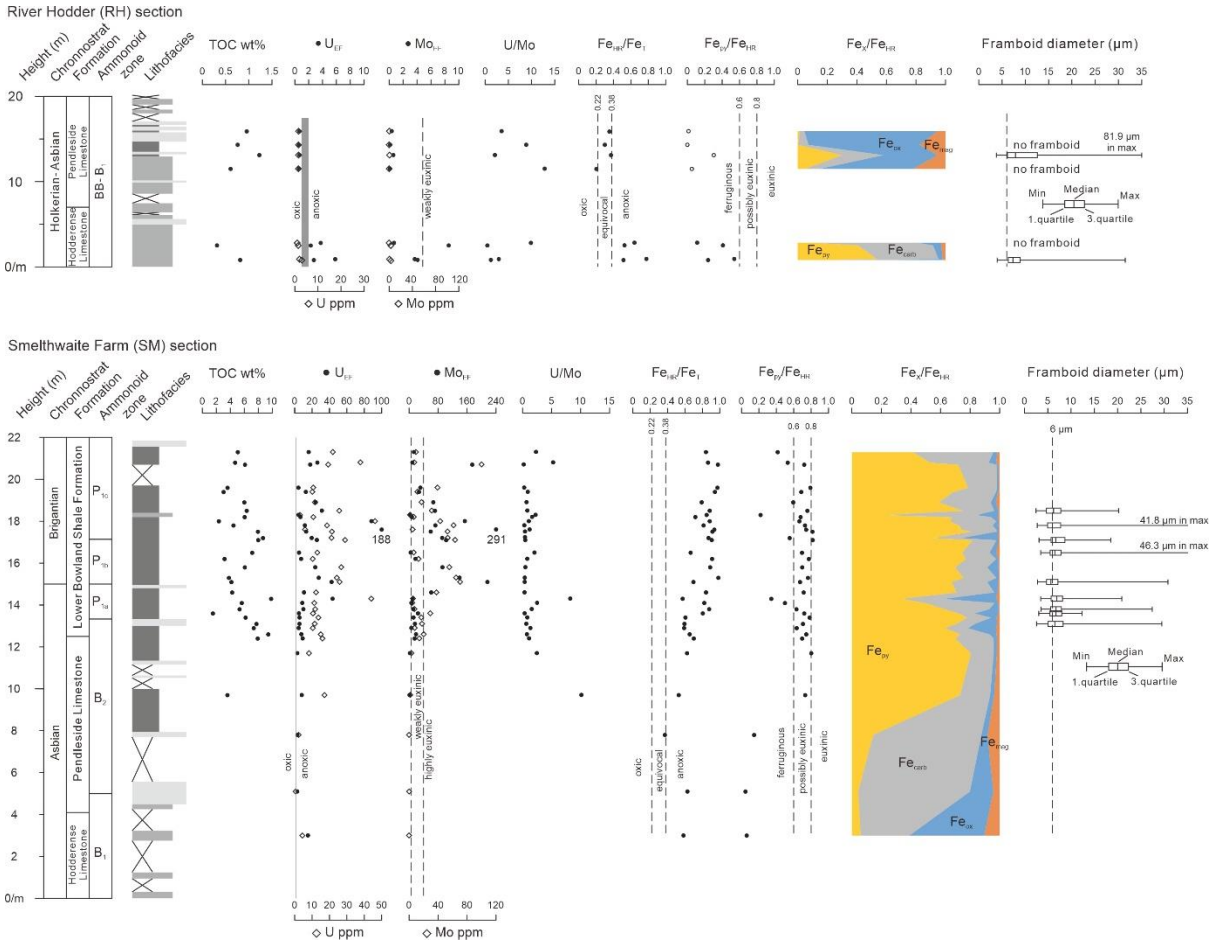

Fig. 4 Geochemical profile for TOC, Fe speciation, trace metal systematics and framboid analyses through the RH and SM sections. The dashed lines on Fe_{HR}/Fe_T plots represent the boundaries for distinguishing anoxic (>0.38) and oxic (<0.22) water column conditions. The dashed lines on Fe_{py}/Fe_{HR} plots indicate the boundaries for distinguishing euxinic (>0.8) and ferruginous (<0.6) water column conditions, and the open circles reflect oxic samples (determined via combined consideration of Fe speciation and trace metal systematics), while closed circles represent anoxic samples. In U and Mo plot, black circles and the diamonds present enrichment factors and concentration respectively and diamonds are only shown presenting zero if its concentration is below detection limits. The gray bar and the dash lines indicate calibrated redox thresholds for U_{EF} and Mo_{EF} respectively (see text)

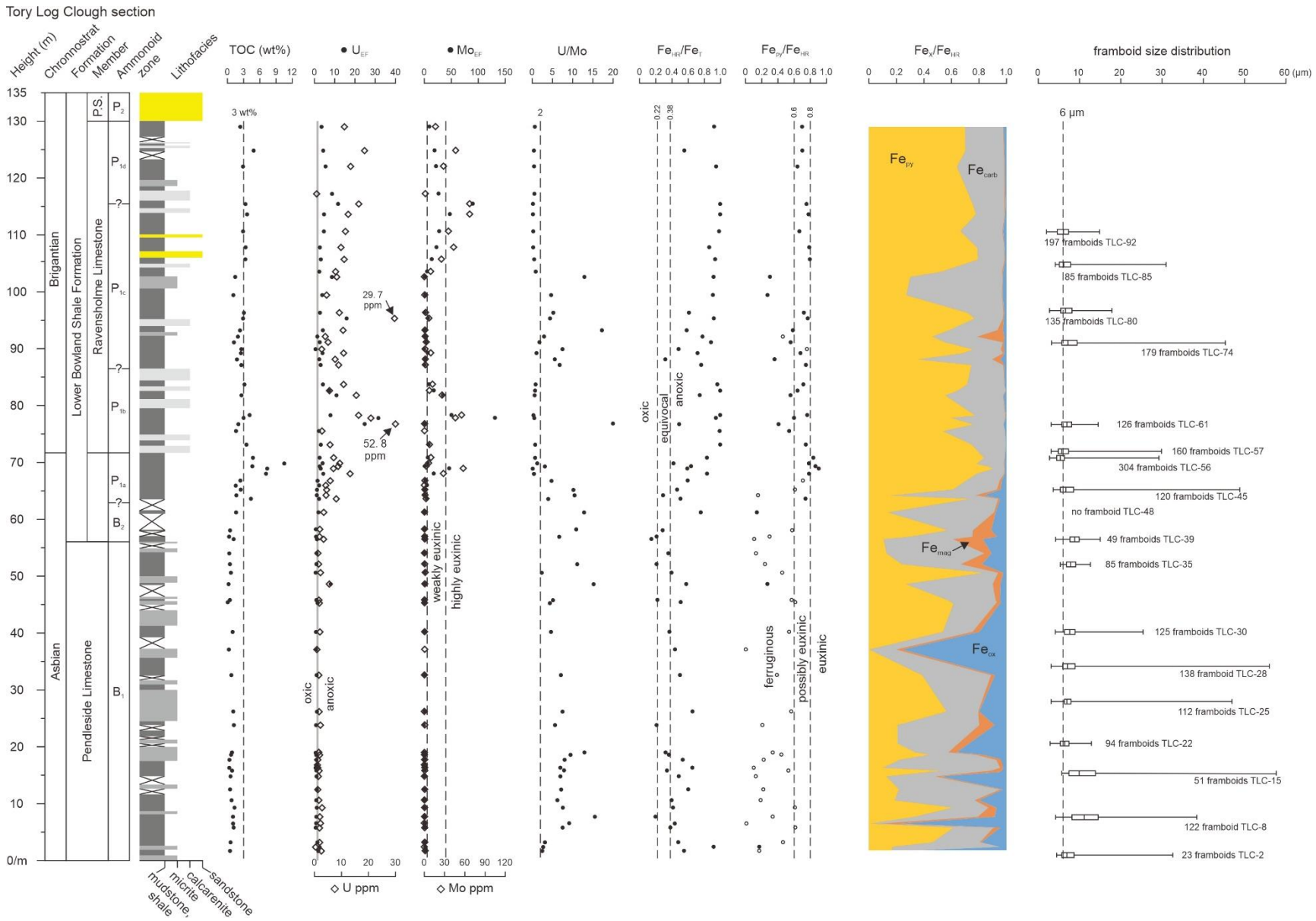

Fig. 5 Geochemical profiles for TOC, Fe speciation, trace metal systematics and framboid analysis at the TLC section. See Fig. 4 caption for additional information.

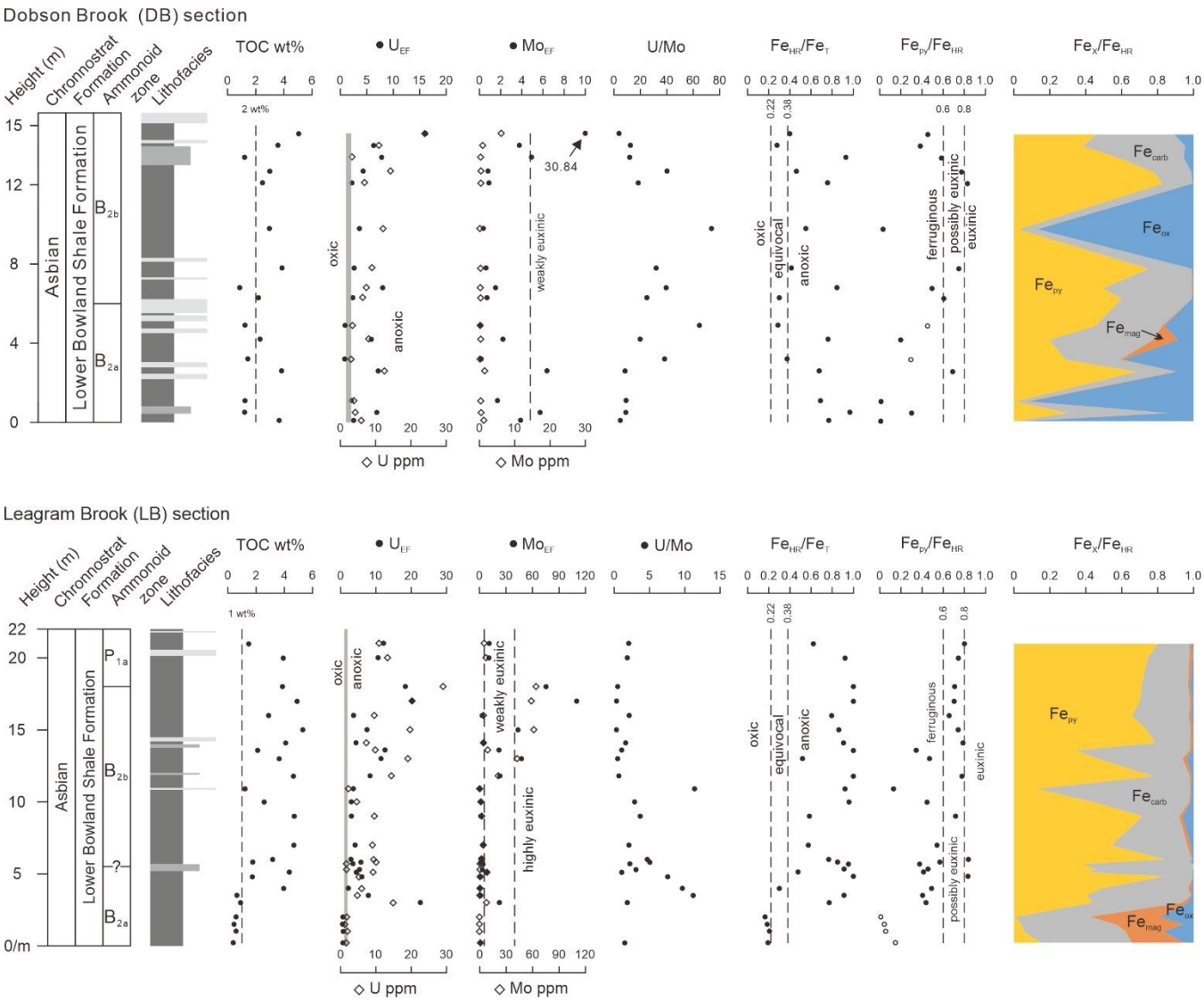

Fig. 6 Geochemical profiles for TOC, Fe speciation and trace metal systematics at the DB and LB sections. See Fig. 4 caption for additional information.

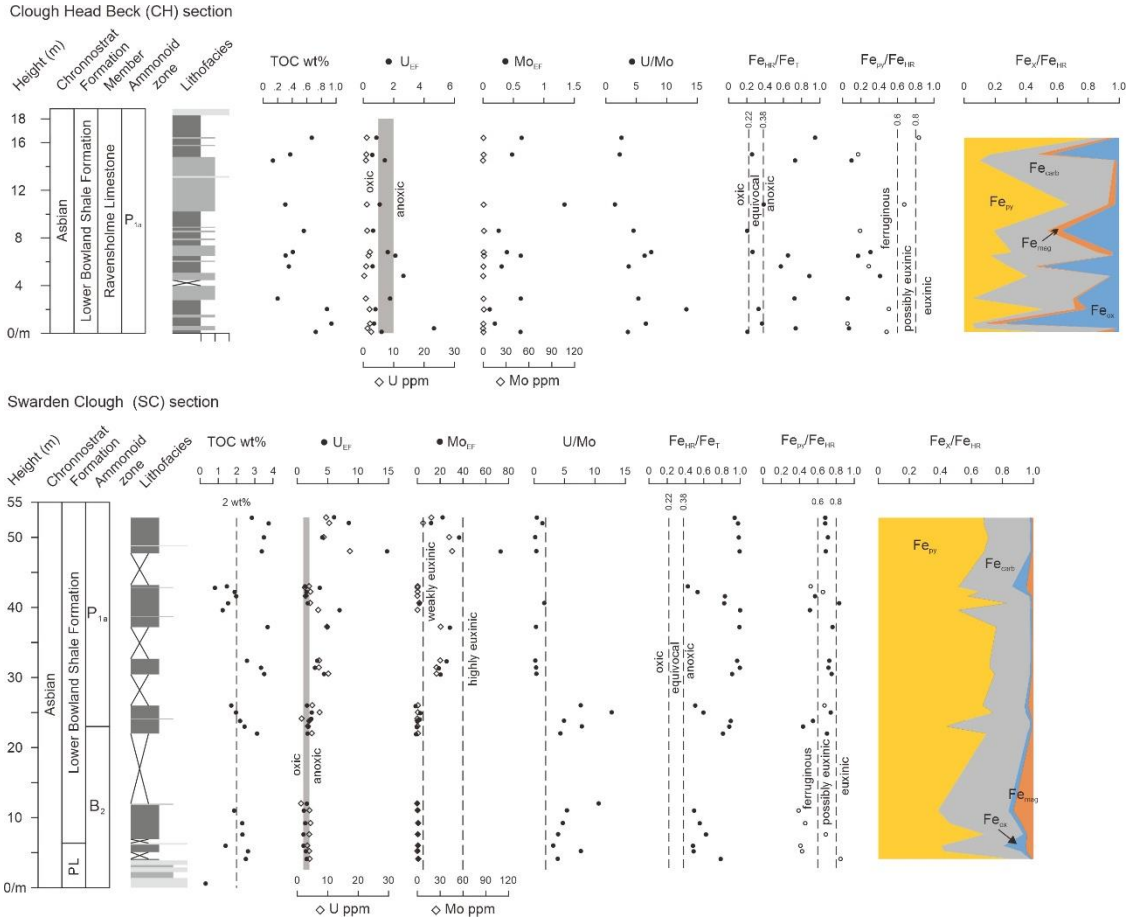

Fig. 7 Geochemical profiles for TOC, Fe speciation and trace metal systematics at the CH and SC sections. PL: Pendleside Limestone Formation. See Fig. 4 caption for additional information.

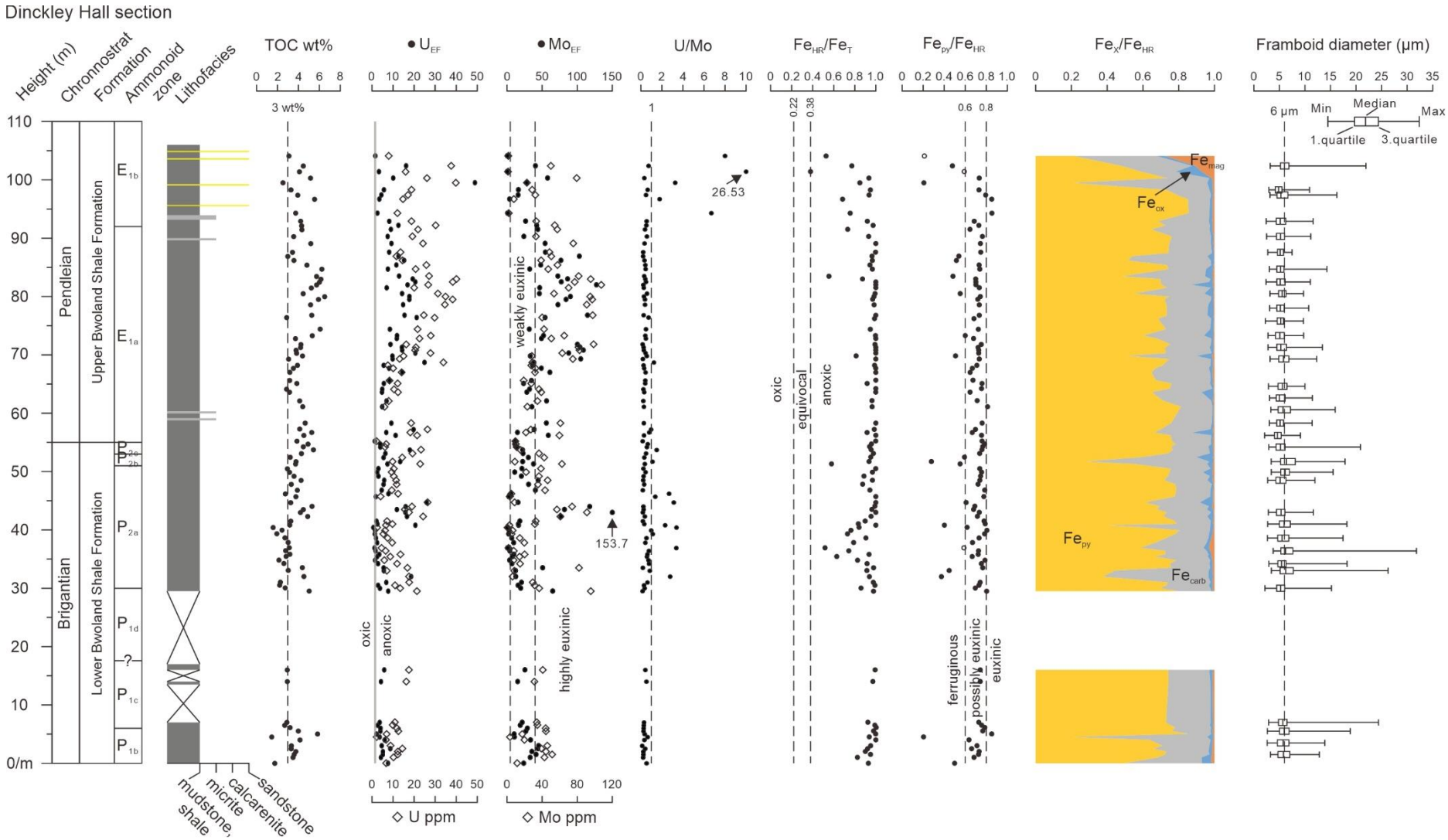

Fig. 8 Geochemical profiles for TOC, Fe speciation, trace metal systematics and framboid analyses at the DH section. See Fig. 4 caption for additional information.

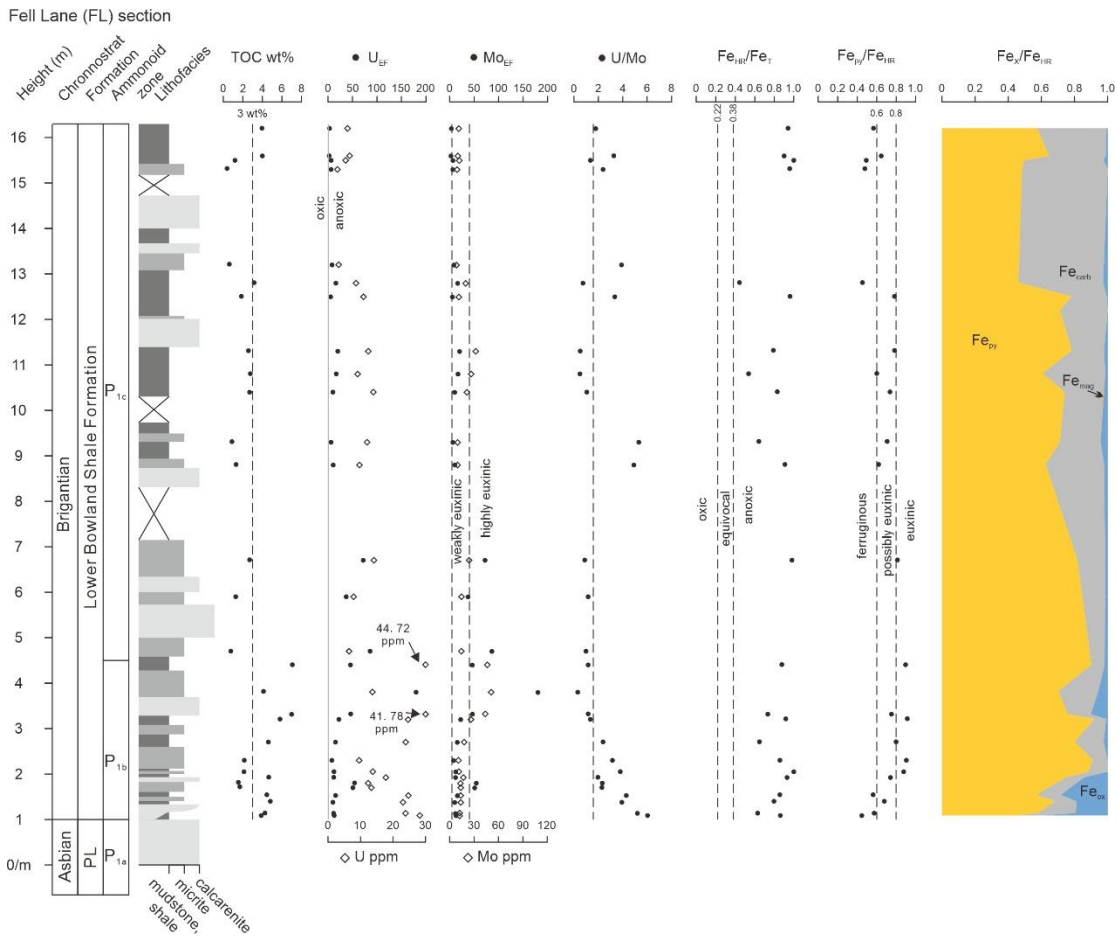

Fig. 9. Geochemical profiles for TOC, Fe speciation and trace metal systematics at the FL section. PL: Pendleside Limestone Formation. See Fig. 4 caption for additional information.

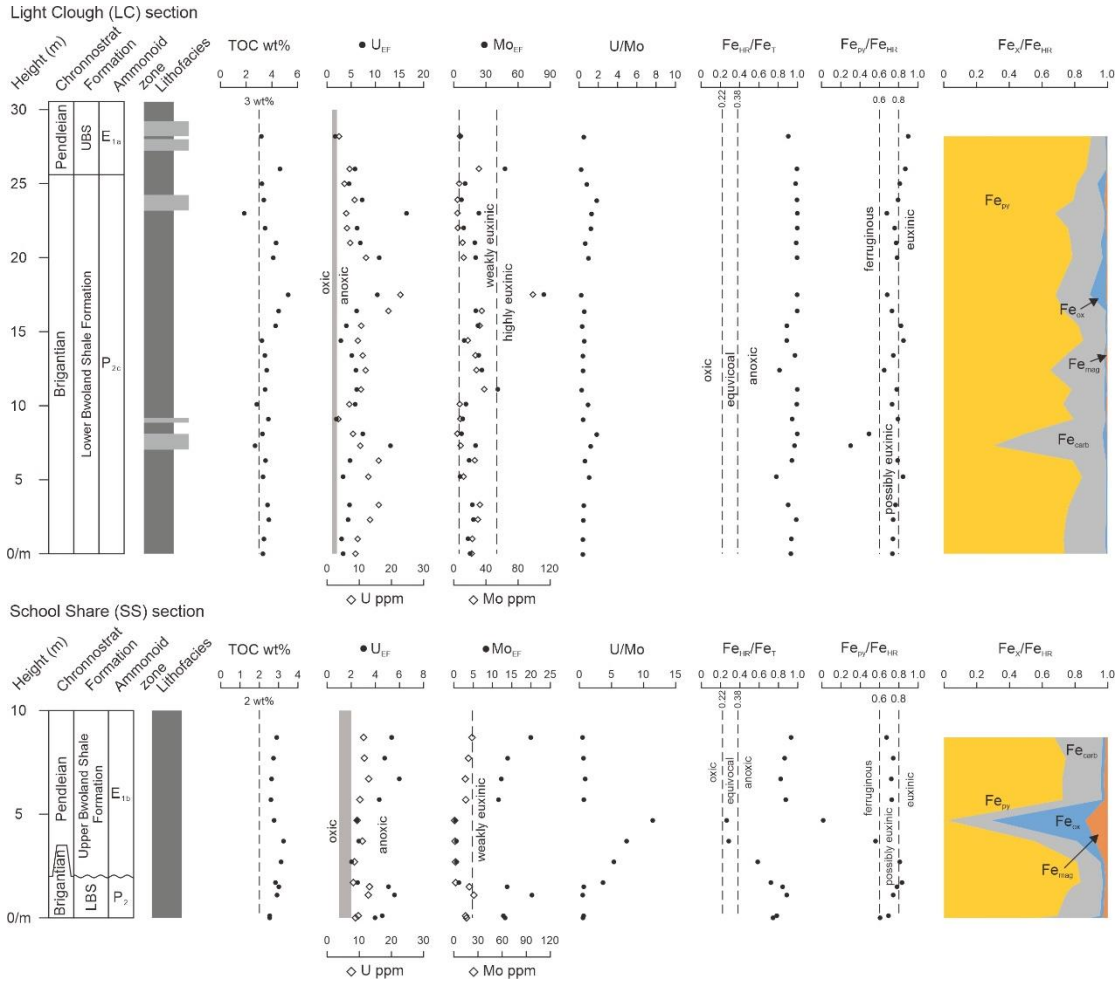

Fig. 10 Geochemical profiles for TOC, Fe speciation and trace metal systematics at the LC and SS sections. LBS: Lower Bowland Shale Formation; UBS: Upper Bowland Shale Formation. See Fig. 4 caption for additional information.

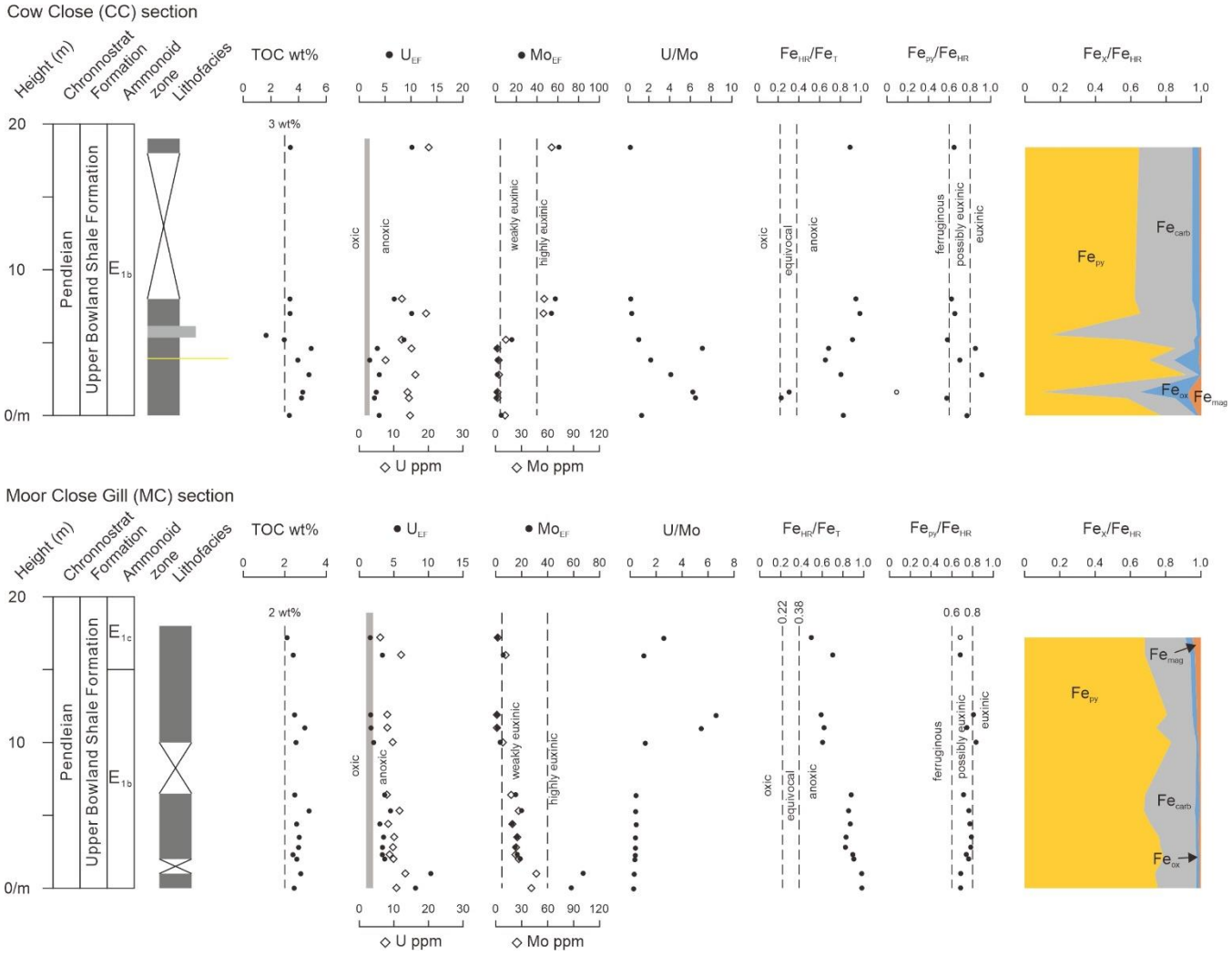

Fig. 11 Geochemical profiles for TOC, Fe speciation and trace metal systematics through the CC and MC sections. See Fig. 4 caption for additional information.

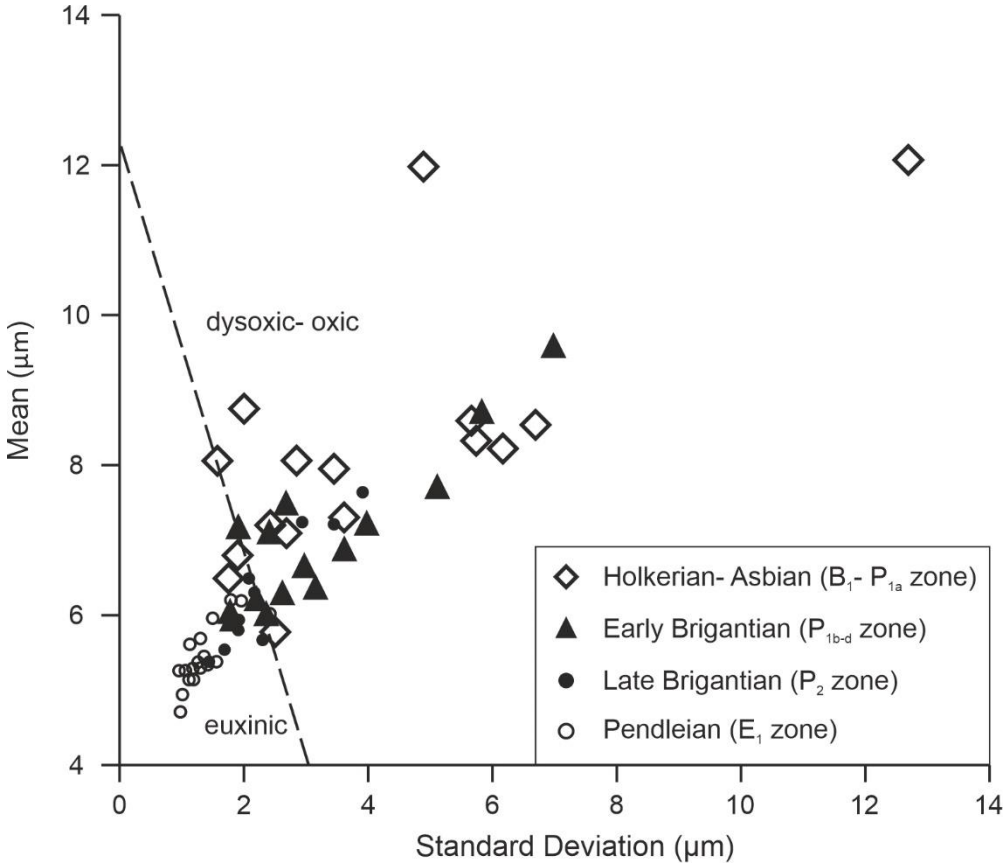

Fig. 12 Wilkin Plot (mean framboid diameter against standard deviation) of framboid populations from the late Holkerian to early Pendleian of the Bowland Basin. Dashed line indicates the euxinic/oxic-dysoxic threshold, as determined in modern environments (Wilkin et al., 1996).

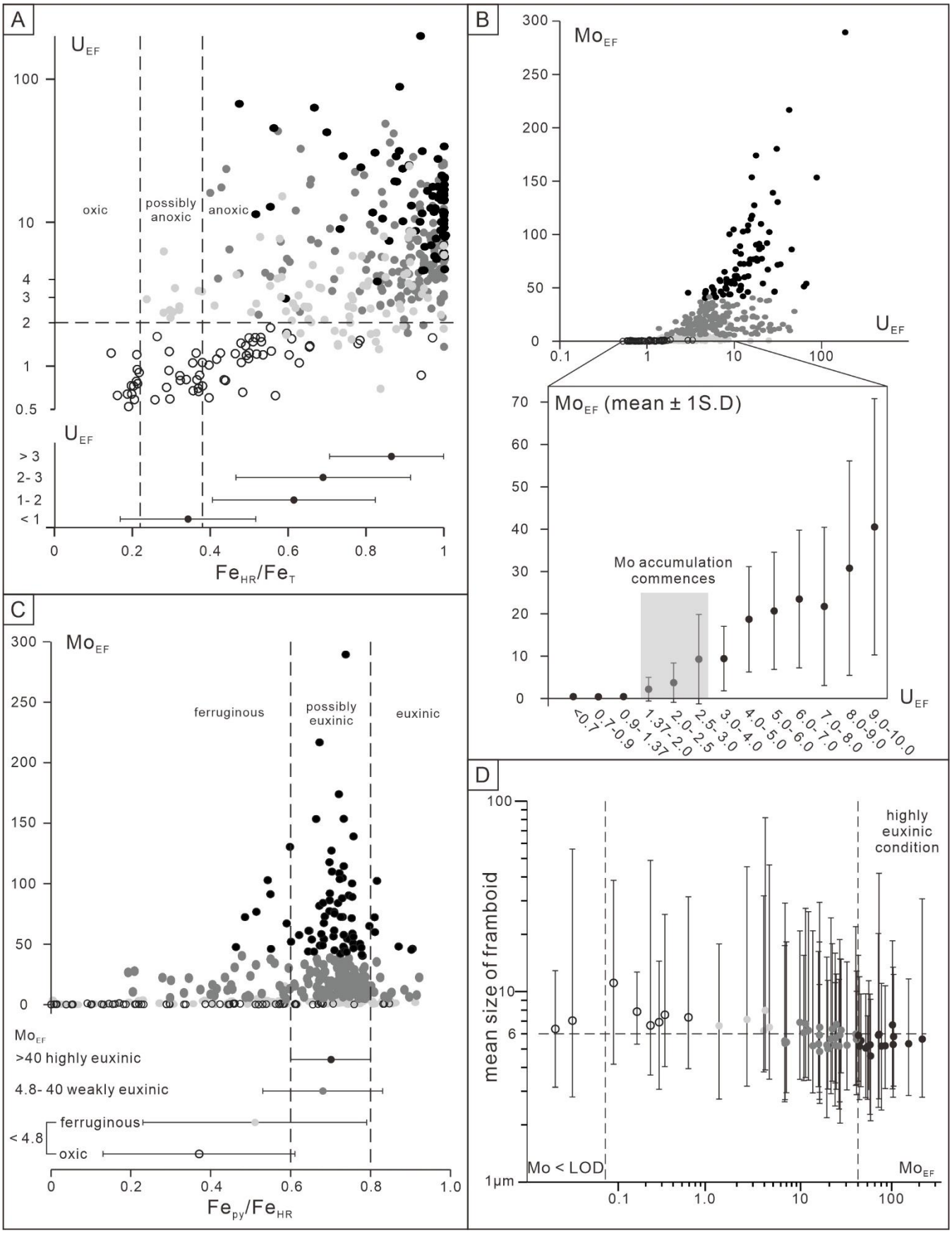
A
U_{EF}
100
10
4
3
2
1
0.5
oxic
possibly anoxic
anoxic
U_{EF}
> 3
2- 3
1- 2
< 1
0
0.2
0.4
0.6
0.8
1
Fe_{HR}/Fe_T
B
Mo_{EF}
300
250
200
150
100
50
0
0.1
1
10
100
U_{EF}
Mo_{EF} (mean ± 1S.D)
70
60
50
40
30
20
10
0
Mo accumulation commences
U_{EF}
<0.7
0.7-0.9
0.9-1.37
1.37-2.0
2.0-2.5
2.5-3.0
3.0-4.0
4.0-5.0
5.0-6.0
6.0-7.0
7.0-8.0
8.0-9.0
9.0-10.0
C
Mo_{EF}
300
250
200
150
100
50
0
ferruginous
possibly euxinic
euxinic
Mo_{EF}
>40 highly euxinic
4.8- 40 weakly euxinic
< 4.8
ferruginous
oxic
0
0.2
0.4
0.6
0.8
1.0
Fe_{py}/Fe_{HR}
D
100
10
6
1μm
mean size of framboid
highly euxinic condition
Mo < LOD
Mo_{EF}
0.1
1.0
10
100

Fig. 13 Redox threshold calibrations based on proxy covariation; open, light gray, dark gray and black circles illustrate oxic, ferruginous, weakly euxinic and highly euxinic samples. (A) U_{EF} and Fe_{HR}/Fe_T cross plot, upper part showing data points and lower part showing statistical analysis in which Fe_{HR}/Fe_T data are displayed as mean values (± 1 S.D), where U_{EF} is <1, 1-2, 2-3 and >3. (B) Mo_{EF} and U_{EF} cross plot and its corresponding statistical analysis showing there is no Mo accumulation with U_{EF} <1.37, but that Mo enrichment increases rapidly as U_{EF} increases above 3.0. (C) Mo_{EF} and Fe_{py}/Fe_{HR} cross plot showing scattered Fe_{py}/Fe_{HR} ratios for oxic and ferruginous samples, but with Fe_{py}/Fe_{HR} ratios dominantly falling in and above the possibly euxinic zone when Mo_{EF} is > 4.8. (D) framboid size distribution (points refer to mean value, and upper and lower limits represent the maximum and minimum framboid diameters) and Mo_{EF} cross plot showing a broad decline in framboid size as Mo_{EF} increases. Large framboids (mean value > 6 μm) occur when Mo_{EF} is below 10, while framboid mean sizes < 6 μm commonly occur with Mo_{EF} > 10. With Mo_{EF} > 40, all framboid populations are < 6 μm in mean diameter. LOD: limit of detection.

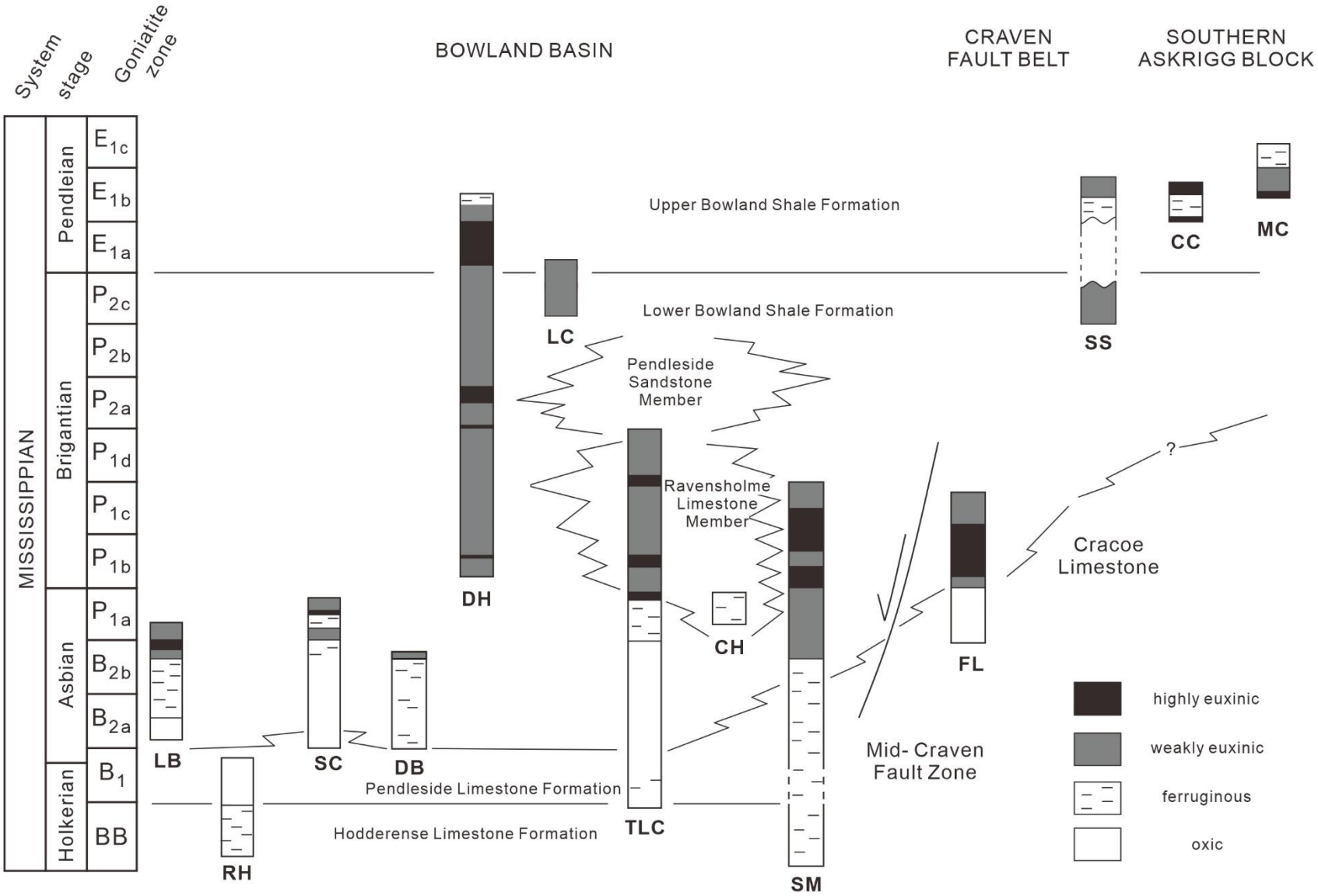

Fig. 14 Summary of the redox history of the Bowland Basin study sites showing a gradual increase in the extent and intensity of anoxia from the Asbian to the early Pendleian. The extent of Bowland Shale deposition also increases with onlap of the marginal Craven Fault Belt beginning in the Brigantian and extending onto the Askrigg Block in the late Brigantian- Pendleian.

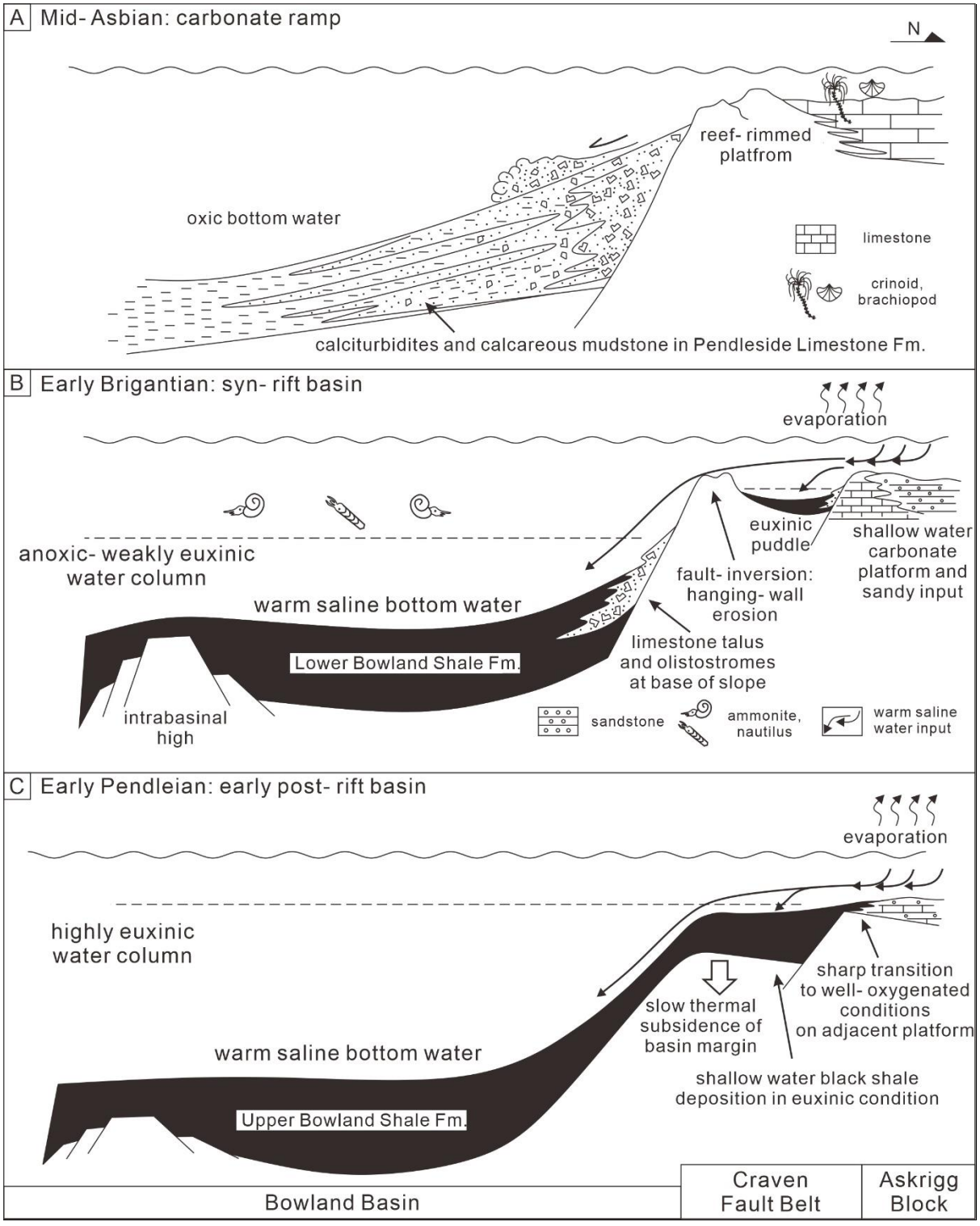

Fig. 15 Depositional model for the development of the Bowland Shale Formation from a carbonate ramp experiencing little oxygen restriction in the mid Asbian, to a fault-bounded syn-rift basin in the Brigantian with ferruginous-euxinic bottom waters, to a post-rift basin experiencing flank collapse and onlap of black shales onto the basin margin in the early Pendleian. Euxinic waters are envisaged to have been maintained beneath a salinity stratified water column in which warm saline bottom waters, generated on adjacent carbonate shelves, supplied the deep water.

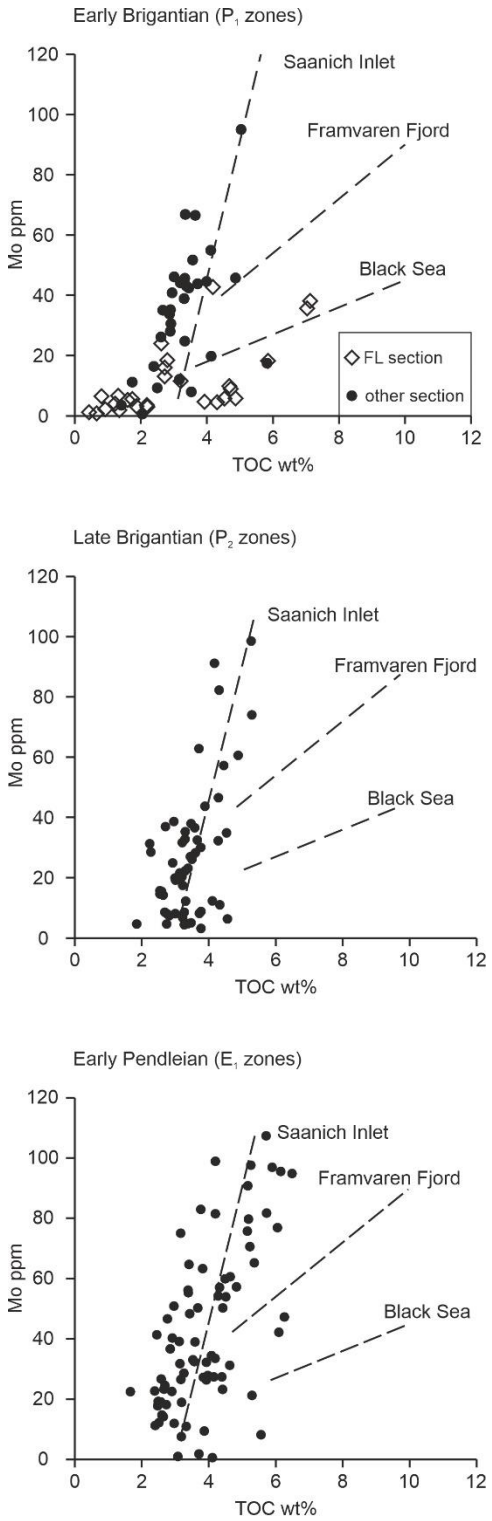

Fig. 16 Mo/TOC plots from the Brigantian to Early Pendleian in the Bowland Basin (dashed lines depict gradients from three modern, silled anoxic basins; Algeo and Lyons, 2006).