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Pyrite framboid size distribution of the Grey Shales (Yorkshire UK) as an indication of redox conditions

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Abstract: *The pyrite framboid size distribution of 26 samples from the Grey Shales were analysed to determine the water column redox history of the sediments. The pyrite framboids range from 4.46μm to 8.76μm in diameter which is indicative of framboids nucleation and growth within an oxic to dysoxic water column. In contrast to the higher oxygenation shown by the framboid size distribution pattern, the paleoecologies of the sediments indicate severe depletion of oxygenated conditions. This variance may have been due to a fluctuating redox interface leading to brief periods of oxygenation or size sorting from storm events that probably favoured the preservation of larger size framboids.*
Keywords; *Pyrite framboid, Grey Shales, Size sorting, Anoxic environment.*

I. Introduction

Pyrite framboids are densely-packed, raspberry–like, spherical aggregates of equigranular micron-sized pyrite crystals which range from a few microns to several tens of microns in diameter. Wilkin and Barnes[1] suggest that they are formed through a four stage process; nucleation of iron monosulphide microcrysts ; reaction of microcrysts to greigite (Fe_3S_4); aggregation of greigite microcrysts into densely packed, spherical clusters and conversion of greigite to pyrite. Reducing conditions are required in the first and fourth reaction whilst the second requires weakly oxidizing conditions [2]. Framboids form near the redox interface (transition from oxic to anoxic) and this could either be in the sediments or within the water column. For oxic marine conditions, framboids form within the sediments near the sediment water interface where the oxidant required for the second step can be acquired from bacterial sulphate and iron reduction [3]. In euxinic basins however, framboids form within the water column directly beneath the redox boundary and this places a limitation on their size as they are unable to attain appreciable sizes before they sink to the seafloor [4].

Wilkin *et al.* [3], based on a detailed survey of the size distribution of pyrite framboids in recently deposited sediments in euxinic, dyoxic and oxic environment concluded that framboids formed in modern euxinic basins were on the average smaller (<5μm in diameter; Fig 4a) and less variable in size than those formed in modern sediments underlying oxic water columns and as such proposed that framboid size distribution may be used for evaluating bottom water redox conditions of fine grained sedimentary rocks. Wilkin *et al* [5] also noted that euxinic framboids show no evidence of enlargement once they have accumulated within the sediment, though infilling and overgrowth might occur. Studies of the size distribution pattern of pyrite framboids from paleoecologically-determined, oxygen-restricted biofacies in selected British Jurassic black shales [4] affirm that the size distribution of framboids is an excellent indicator of ancient redox conditions and the parameter (small framboids with a narrow size distribution) is especially diagnostic of euxinic conditions. In this paper, the size distribution of framboids from the Grey Shales member of the Whitby Mudstone Formation (Cleveland Basin, United Kingdom) are reported and discussed in the light of Wilkin's predictions.

II. Geological Setting

The Grey Shales are exposed in cliffs along the North Yorkshire coast and is the lowest member of the Withby Mudstone Formation (Fig. 1). The rocks are Lower Toarcian in age and were deposited in the Cleveland Basin. The Grey Shales comprises of three thin laminated black shales (beds 26, 2 and 19 of Howarth [6]) separated by silty bioturbated mudstones and overlain by the Jet Rock. The lowest of these black shale units have been termed the 'Sulphur Band' [7] on the basis of its yellowish sulphurous appearance caused by the weathering of its abundant pyrite content. At Staithes, the shale units occur approximately at 0.4, 1.5 and 5.4m above the base of the Grey Shales and have been termed the Lower, Middle and Upper Sulphur Bands respectively [8]. Since this study looks at the laminated black shale units within the Grey Shales these terminologies will be used throughout the text. The Middle Sulphur Band (MSB) is different from the other Sulphur Band units. It is thicker and has a bioturbated shaley layer in the middle showing an increase in bottom water oxygenation.

Hallam [9], describes the Grey Shales, Jet Rock and the Alum Shale members of the Whitby Formation as sediments deposited during a period of marine transgression. The Grey Shales was deposited under shallow marine conditions; this is evident by the diversity of benthic taxa found within the bioturbated sections. Although, a diverse assemblage of benthic organism is present in the mudstones of the Grey Shales, Newton [8] observed that the Sulphur Bands in contrast, record a complete loss of benthos. Wignall [10] reports the presence of *Chrondrites* and *Diplocraterion* (ichnofossils normally associated with shallow water deposition) on the top of the lower Sulphur Band as well as the presence of storm scours in the Sulphur Bands.

<table>
<tr><th rowspan="2">STAGE</th><th colspan="3">LITHOSTRATIGRAPHIC UNITS</th></tr>
<tr><th>GROUP</th><th>FORMATION</th><th>MEMBER</th></tr>
<tr><td rowspan="5">TOARCIAN</td><td rowspan="6">LIAS</td><td rowspan="5">WHITBY MUDSTONE</td><td>Fox Cliff Sandstone</td></tr>
<tr><td>Peak Mudstone</td></tr>
<tr><td>Alum Shale</td></tr>
<tr><td>Jet Rock</td></tr>
<tr><td>Grey Shales</td></tr>
<tr><td>PLIENNSBACHIAN</td><td colspan="2">CLEVELAND IRONSTONE</td></tr>
</table>

Figure 1. Lithostratigraphy of the Grey Shales

III. Analytical Method

Samples were taken from Hawsker Bottoms along the Yorkshire Coast of Northern England. 26 whole-rock samples, each sawed perpendicular to the bedding plane were mounted in resin blocks, polished and given a light gold coating. The samples were viewed under a scanning electron microscope (SEM) at a magnification of x2670 using the back scattered electron mode to distinguish the pyrite framboids. The size of pyrite framboids was measured directly from the SEM screen to the nearest 1µm using a ruler calibrated in µm at the above magnification. This method tends to underestimate the true diameter of the framboids when not measured in the median section, however, calculation shows that the deviation from the true mean diameter is unlikely to exceed 10% [3]. A minimum of 100 framboids were measured in each polished thin section in other to achieve stable size distribution statistics.

IV. Results

Four types of pyrite were identified during the SEM work on the Sulphur Band samples, namely (1) Typical framboids; closely packed spherical aggregates of uniform-sized microcrysts (Fig.2a), (2) Framboids consisting of less densely packed microcrysts with a greater range of microcryst size within the framboid (Fig.2b), (3) Aggregates of pyrite crystals normally in the size range of framboids but consisting of overgrowths and so the microcrysts lack uniformity (Fig.2d), (4) Diagenetic pyrite crystals occurring either as single euhedral crystals or in clusters or as irregularly shaped mass (Fig.2c). the framboids also occurred in clusters and rings (Fig. 2e) Measurements were only taken across framboids with typical size and shape, as they were in the majority.

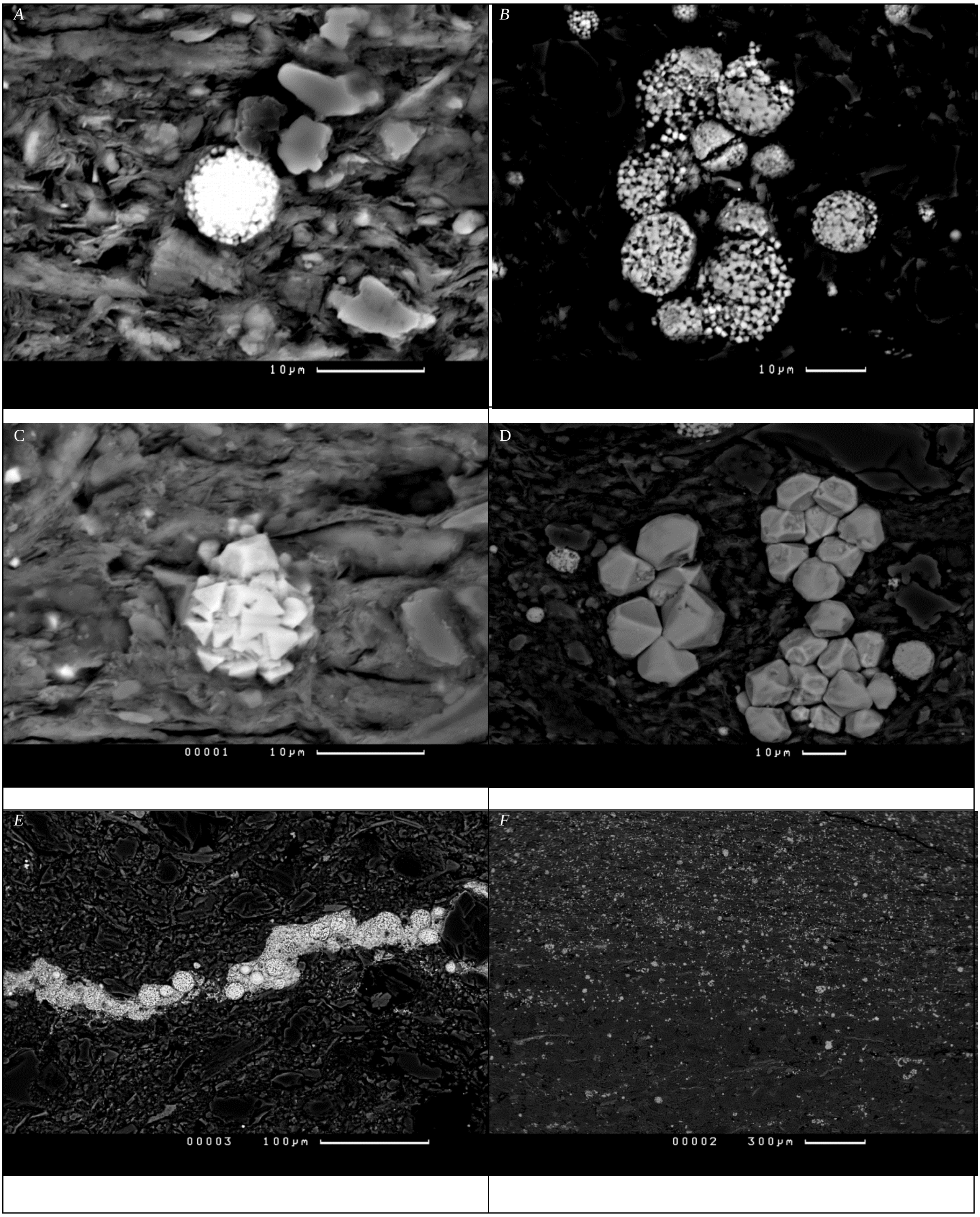

Figure 2. Backscatter SEM images of (a) typical framboid. (b) framboids showing looser packing of microcrysts (c) aggregates of pyrite packed as framboids (d) Individual euhedral pyrite crystals in a cluster (e) framboids occurring as clusters formed in a ring (f) different framboid population between shaley and silty laminae

Table 1. Statistical data of the measured pyrite framboids

Sample Name	No. Of Framboids Measured	Mean	Standard Deviation	Maximum Framboid Diameter	Skewness
NSB-LSB-1/2	105	8.76	4.60	30	0.50
NSB-LSB-4/5	50	7.36	3.12	18	0.35
NSB-LSB-6/7	119	8.48	4.85	28	0.92
NSB-LSB-10/11(i)	148	7.18	3.79	21	0.94
NSB-LSB-10/11(ii)	120	4.49	2.18	17	0.68
NSB-LSB-13/14	126	5.94	3.13	20	0.90
NSB-LSB-18/19	116	5.60	2.29	15	0.79
NSB-LSB-19/20	118	7.13	2.10	13	0.18
NSB-MSB-11	134	4.75	2.84	30	0.80
NSB-MSB-12	128	4.66	1.80	12	1.10
NSB-MSB-13	131	5.64	2.55	17	0.75
NSB-MSB-21	135	5.18	2.42	22	0.22
NSB-MSB-27	131	5.71	2.87	17	0.74
NSB-MSB-28	123	5.24	2.61	23	0.28
NSB-MSB-30	135	4.78	1.57	12	-0.43
NSB-MSB-32	125	5.74	1.87	13	-0.41
NSB-MSB-37	122	4.73	2.27	18	0.96
NSB-MSB-45	115	6.01	2.98	22	1.01
NSB-USB-2cm B1	111	6.15	3.55	28	0.97
NSB-USB-4/5	120	7.03	3.28	24	0.94
NSB-USB-9	146	5.51	3.54	25	0.44
NSB-USB-10	140	6.11	2.91	18	1.14
NSB-USB-11/12	143	5.33	3.07	24	0.32
NSB-USB-14/15	179	6.75	2.70	22	0.84
NSB-USB-17	136	4.82	2.08	13	1.18
NSB-USB-19/20	132	5.00	2.99	22	1.00

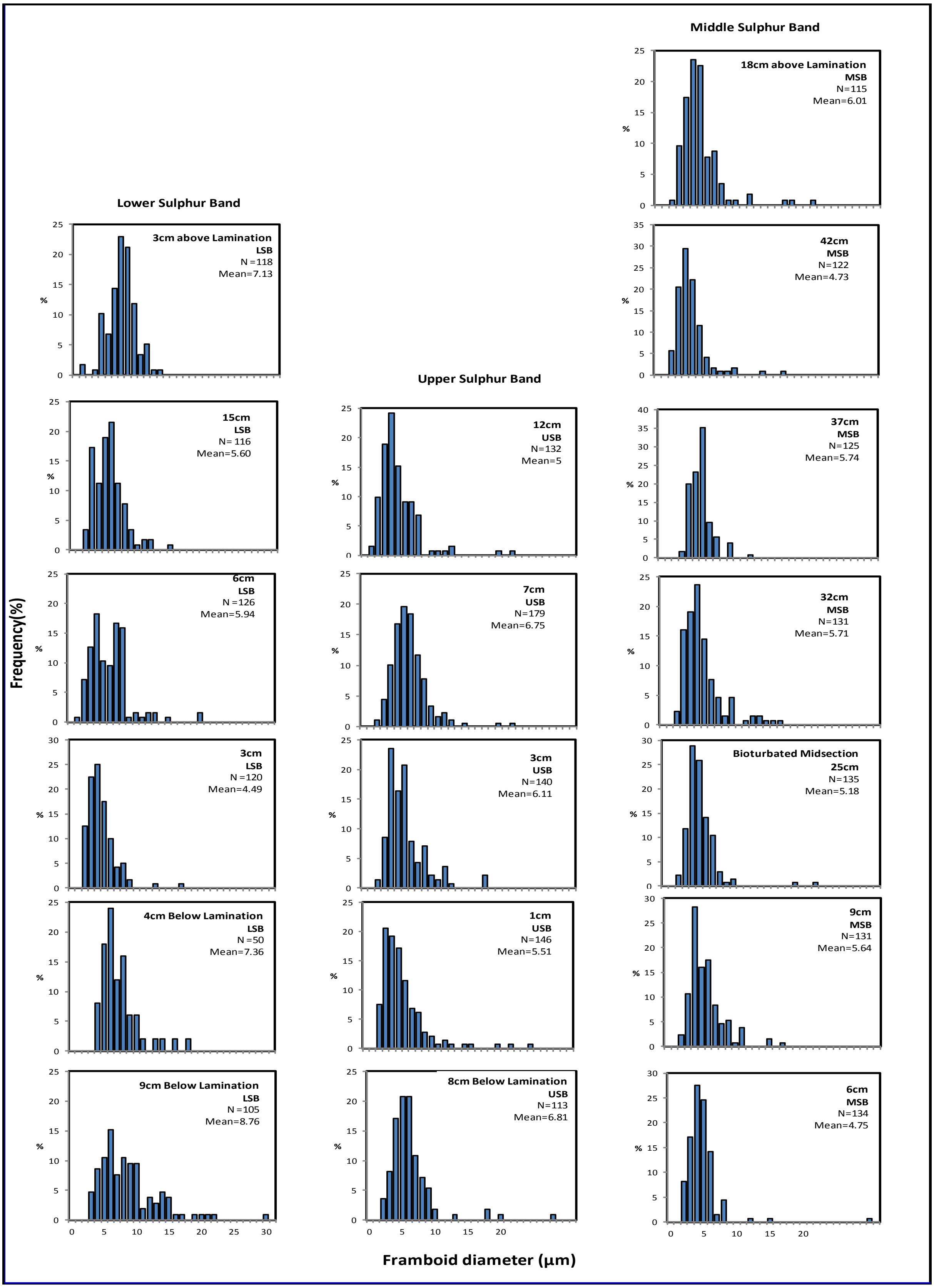

Figure 3. Histograms showing size distribution frequency of pyrite framboids from the Sulphur Bands as a function of their position from the base of the lamination.

Statistics of the framboid size distributions (mean, standard deviation about the mean, maximum framboid diameter, number of framboids measured per sample, skewness) are listed in Table 1. Histograms plots of the size distribution of the Sulphur Bands had sharp peaks and extended tails (Fig. 3). The samples show varied mean diameters which ranged from 4.46μm to 8.76μm. Framboid diameters above 30μm occur very rarely (though some samples contained up to 3) and were not included in the frequency distribution of the samples where they occur. Newton [8] suggests that these larger framboids were formed in an environment with low sedimentation rate and more oxic conditions which are different from the modern environment [3] to which the samples are being compared with. These large framboids would enormously increase the standard deviation of the size distribution and so would not fit into the model. Samples taken from the bioturbated mudstones immediately below and above the lower Sulphur Band (LSB) contained more of framboids with overgrowths than typical framboids. In general, samples from the bioturbated sections directly above and below the Sulphur Bands had typical framboids with mean diameter of about 7.9μm and contained less framboids than the Sulphur Band samples. The maximum framboid diameters measured from the bioturbated sections were also higher. However, for the MSB, samples from the bioturbated top of the bed did not vary much from samples from the laminated sections.

V. Discussion

Figure 4 shows the size distributions of the Sulphur Bands and compares it with plots from modern environment after Wilkin et al., [3]. The plot of mean versus the standard deviation of Lower Sulphur Band and Upper Sulphur Band (USB) position them on the oxic-dysoxic side of the redox boundary. The Lower Sulphur Band is marked by the disappearance of all fossil remains, except for exceptionally rare fragments of dactylioceratid ammonites [8], and the development of lamination indicating severe depletion of oxygenated conditions during the deposition. The Upper Sulphur Band on the other hand records a complete loss of benthic fauna but does contain the occasional ammonite, suggesting the existence of permanent water anoxia that did not necessarily extend high into the lower water column. The mean diameter of the framboids measured from these units ranged from 5-8μm and are more suggestive of oxic–dysoxic environment. This is inconsistent with their paleo-ecology. A look at the sedimentary fabric of the LSB reveals that it is a silt laminated black shale with the silt laminae towards the top exhibiting very low angle hummocky cross stratification [10], suggesting it was affected by storm events. Such a storm event responsible for the silt laminae would have temporarily oxygenated the sea floor moving the location of the framboid formation from the water column to the sediment (beneath the redox boundary). Framboids formed within the sediments are typically larger in diameter (> 7μm) than those formed within the water column and this explains the larger diameter sized framboids present in the LSB. Raiswell et al., [11] described size sorting as a process that could explain the preservation of the larger framboids. Size sorting, explained as the winnowing or preferential removal of the smallest diameter framboids, could have occurred during the emplacement of the hummocky cross stratified silt laminae. One of the samples (NSB-LSB-10/11), interestingly clearly shows the transition from shale to silt and measurements were taken across both laminae. The silt laminae had framboids with mean diameter of 7.18μm which is at variance with the mean diameter recorded in the shaley laminae (4.49μm). The shaley laminae also had a larger proportion of framboids when compared to the silty laminae (Fig. 2f) indicating loss of framboids in the silt laminae. This clear record of disparity between the framboid size diameters of both laminae implies that the LSB framboid size distribution may have been altered by the effect of oxygenation and size sorting. Newton [8] in using various paleo indices to describe the water column anoxia of the Grey Shales noted that the framboid analyses of the LSB and USB do not agree with their Degree of Pyritization and Indicator of Anoxicity values. These paleoredox indices indicate higher degree of anoxia while the framboid data as discussed above records much higher level of oxygenation. Based on the bimodal appearance of some Grey Shale framboid distribution (Fig 3), He suggested a fluctuating redox interface between a position somewhere in the water column and one at the sediment surface. This fluctuating redox conditions in the water column is consistent with the observed framboid distribution of the LSB and USB. Tyson and Pearson [12] pointed out that the onset of widespread anoxia in a laterally extensive epicontinental sea would effectively sterilise the seabed making its recolonisation slow. This might explain the absence of fauna in the fossil record of the Sulphur Bands under periodic anoxia. A fluctuating redox condition in the water column is also true for the framboid size distribution of the MSB. The framboid size data for the Middle Sulphur Band plot in a manner that varies between euxinic and oxic-dysoxic conditions (Fig. 4b). The framboids that plot in the euxinic field (diameters < 6μm) were probably formed in the water column when the bottom waters were anoxic, whilst the others were formed in the sediment when the water column was slightly oxygenated.

The fact that all Sulphur Bands are characteristically laminated, contain abundant organic matter and lacked benthic fauna suggest that the bottom water redox condition at the time of their deposition was anoxic. The presence of silt laminae and the framboid size distribution data of the Sulphur Bands indicates periods of oxygenation, however, the oxygen levels never rose high enough or long enough to allow bioturbating organisms to colonise the sea floor.

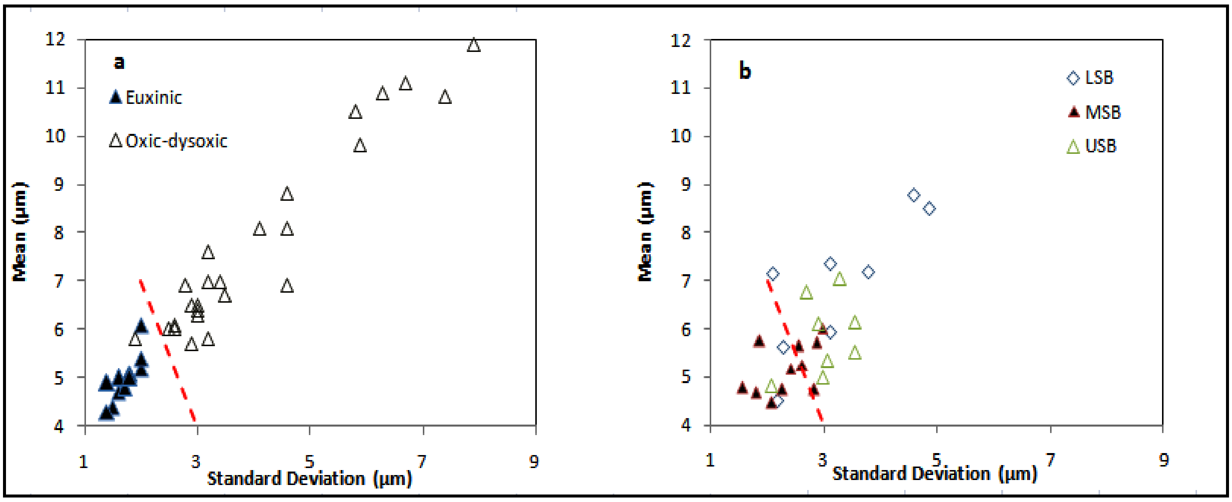

Figure 4. a) Framboid size distribution showing the clear division between framboids from modern euxinic and those from oxic-dysoxic environment (Data from Wilkin et al., 1996). (b) Plot of the mean versus the standard deviation of the framboid size distribution of the samples.

VI. Conclusions

Framboid size distribution analyses of the Sulphur Bands do not give a clear indication of euxinia as suggested by their paleoecology. The lower and upper Sulphur Bands are suggestive of sediments deposited in an oxic-dysoxic environment when compared with modern environment. This may have been due to sedimentary reworking. Framboid data from the middle Sulphur Band suggests a condition varying between euxinia and oxic-dysoxic. . Framboid diameters should be used with care as a paleoredox as discussed above as their size distribution pattern could have been affected by sedimentary reworking. However, when they are used with other paleoredox indices, one could gain understanding of the paleoenvironmental condition of deposition of the sediments.

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