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Sulfur isotope patterns of iron sulfide and barite nodules in the Upper Cretaceous Chalk of England and their regional significance in the origin of coloured chalks

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ABSTRACT :

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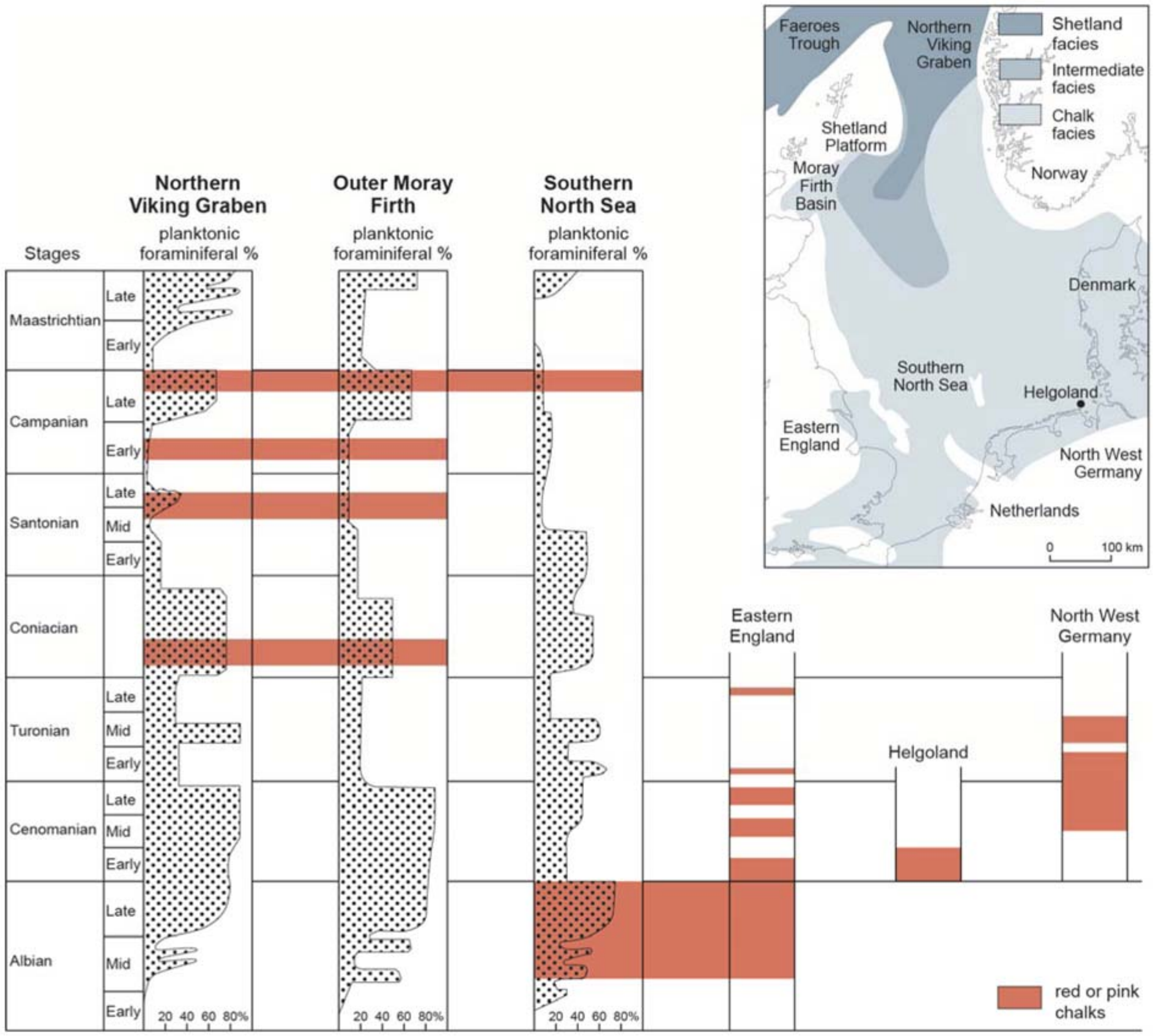
The relationship between the development of iron sulfide and barite nodules in the Cenomanian Chalk of England and the presence of a red hematitic pigment has been investigated using sulfur isotopes. In southern England where red and pink chalks are absent, iron sulfide nodules are widespread. Two typical large iron sulfide nodules exhibit $\delta^{34}S$ ranging from -48.6‰ at their core to -32.6‰ at their outer margins. In eastern England, where red and pink chalks occur in three main bands, there is an antipathetic relationship between the coloured chalks and the occurrence of iron sulfide or barite nodules. Here iron sulfide, or its oxidised remnants, are restricted to two situations: (1) in association with hard grounds that developed originally in chalks that contained the hematite pigment or its postulated precursor $FeOH_3$, or (2) in regional sulfidization zones that cut across the stratigraphy. In the Cenomanian Chalk exposed in the cliffs at Speeton, Yorkshire, pyrite and marcasite (both iron sulfide) nodules range in $\delta^{34}S$ from -34.7‰ to +40.0‰. In the lower part of the section $\delta^{34}S$ vary from -34.8‰ to +7.8‰, a single barite nodule has $\delta^{34}S$ between +26.9‰ and +29.9‰. In the middle part of the section $\delta^{34}S$ ranges from +23.8‰ to +40.0‰. In the sulfidization zones that cut across the Cenomanian Chalk of Lincolnshire the iron sulfide nodules are typically heavily weathered but these may contain patches of unoxidised pyrite. In these zones, $\delta^{34}S$ ranges from -32.9‰ to +7.9‰. The cross-cutting zones of sulfidization in eastern England are linked to three basement faults – the Flamborough Head Fault Zone, the Caistor Fault and the postulated Wash Line of Jeans (1980) – that have affected the deposition of the Chalk. It is argued that these faults have been both the conduits by which allochthonous fluids – rich in hydrogen sulfide/sulfate, hydrocarbons and possibly charged with sulfate-reducing bacteria – have penetrated the Cenomanian Chalk as the result of movement during the Late Cretaceous or Cenozoic. These invasive fluids are associated with (1) the reduction of the red hematite pigment or its praecursor, (2) the subsequent development of both iron sulfides and barite, and (3) the loss of overpressure in the Cenomanian Chalk and its late diagenetic hardening by anoxic cementation. Evidence is reviewed for the origin of the red hematite pigment of the coloured chalks and for the iron involved in the development of iron sulfides, a hydrothermal or volcanogenic origin is favoured.

Key words: Cretaceous; Diagenesis; Iron sulfide nodules: $\delta^{34}S$ values; Bacterial control; Coloured chalks; Volcanogenic events; NW Europe.

INTRODUCTION

Bands of coloured chalks – red to the palest pinks and violets – with their erratic and unpredictable occurrence are an enigmatic feature of the Cretaceous Chalk of the North Sea and the surrounding regions where they range in age from Albian to Campanian (Text-fig. 1). The best known are the onshore examples in eastern England, Helgoland, and in northwest Germany. In eastern England, coloured chalks are found mainly in the mid to Late Albian Red Chalk Formation, the Cenomanian Ferriby Chalk Formation and locally in the basal part (Variegated Beds) of the overlying Late Cenomanian to Turonian Welton Formation (Bower and Farmery 1910; Jeans 1980): they are also present in the Turonian Burnham Chalk Formation (Hildreth 2013). In the North Sea coloured chalks are known from the Late Cenomanian – Early Turonian Blodøks Formation (Voigt *et al*. 2008) and the mid Turonian-Campanian Hod Formation (Hancock 1990, fig. 9.10; Voigt *et al*. 2008) as well as in chalks of Early Coniacian, mid Santonian, and Early and Late Campanian age (Text-fig. 1). Coloured chalks are also present in the Cenomanian Chalk of Helgoland (NW Germany), an island situated in the North Sea approximately 85 km northeast of Bremerhaven (Wood and Schmid 1991). In north Germany, coloured chalks are well known in the Upper Cenomanian and Turonian sequences – the Brochterbeck Formation of Munsterland, Lower Saxony and Saxony-Anhalt and the Rotplänar of Lüneburg, Brandanburg and S.W. Mecklenburg (Voigt *et al*. 2008, fig. 15.13). Wiese (2009) has provided a detailed de-



Text-fig. 1. Distribution of red and pink zones in the Albian and Late Cretaceous (Cenomanian to Maastrichtian) strata in the North Sea, Eastern England, Helgoland and North West Germany. The proportion of planktonic forms in the foraminiferid assemblages is shown for various regions of the North Sea. High values are frequently associated with these coloured zones (based in part on King *et al*. (1989) and unpublished data from Haydon Bailey) scription of the coloured chalks in the Late Cenomanian to Late Turonian Söhlde Formation in the Lower Saxony Basin.

In the Upper Cretaceous Chalk of England there is a general and detailed antipathetic distribution pattern between these colour bands and the presence or absence of iron sulfide minerals, such as pyrite, or marcasite. The colour bands – ranging from dark red and reddish brown through to pale pink, pale purple and pale ochre – are restricted to the Northern Province where they are present in the Cenomanian Ferriby Chalk Formation although there are traces at higher stratigraphic levels (Hildreth 2013, p. 179). The colouring agent is a finely divided hematitic or hydrated iron-oxide pigment, which when diluted with white chalk and small amounts of dark organic matter, produces the range of colours that are present. Evidence for the origin of this pigment comes from the mid to Late Albian Red Chalk (Hunstanton Limestone) Formation that immediately underlies the Upper Cretaceous Chalk in eastern England.

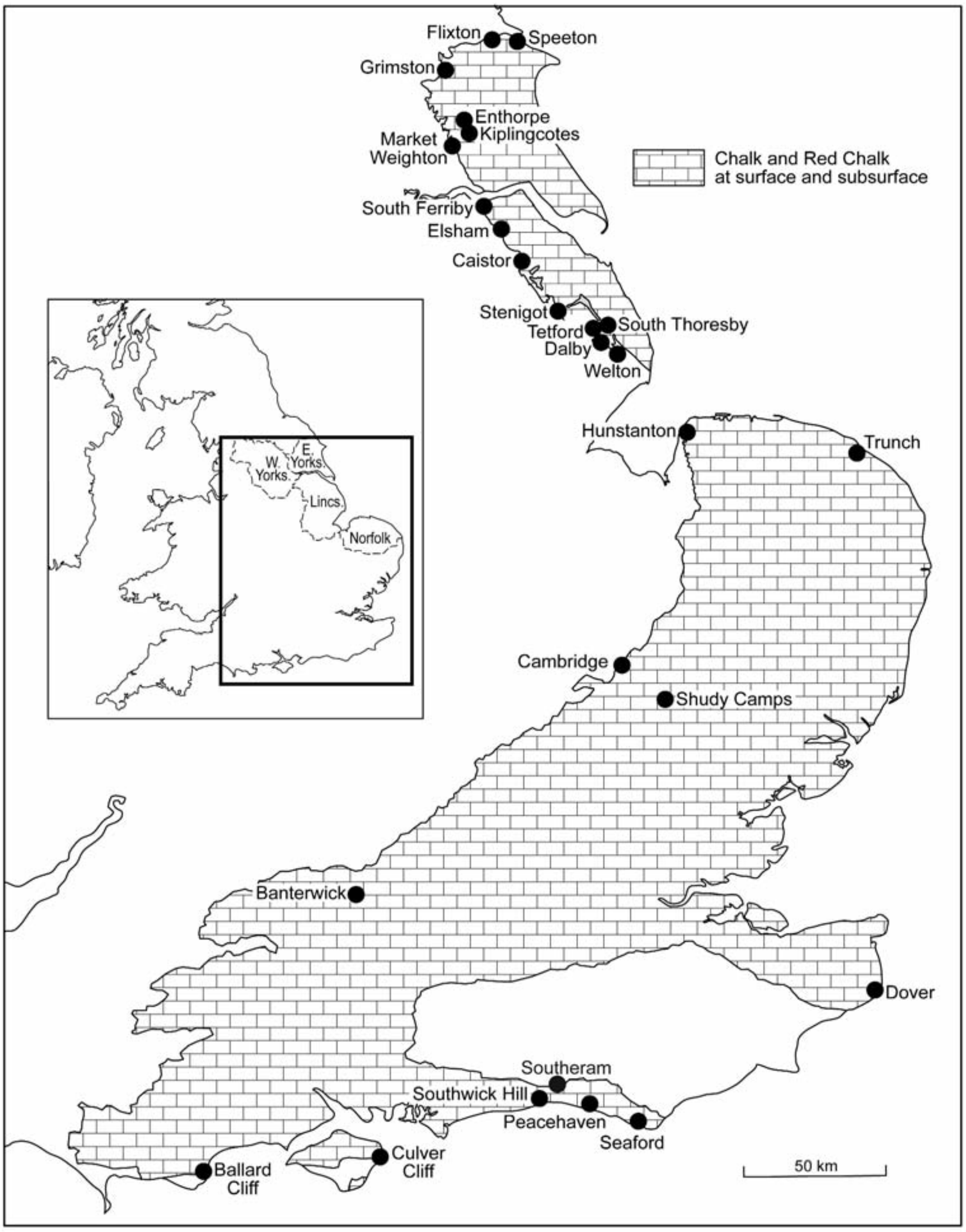
Two iron sulfide minerals, pyrite and marcasite, occur in the Chalk, both are of diagenetic origin formed within the sediment after its deposition. Pyrite, a cubic mineral, is by far the most frequent although it is usually misidentified as marcasite when it occurs in its common nodular form. The dense brown nodules of iron sulfide minerals from the Chalk that are frequently washed out and accumulate in the intertidal zone below Chalk Cliffs – often referred to as "thunderbolts" or "meteorites" by the public – are still frequently misidentified as marcasite although they are pyrite. For example, Bannister (1932) made a thorough study of a selection of nodules from the Cenomanian Lower Chalk at Folkestone using X-ray diffraction and optical microscopy and identified only pyrite; marcasite is orthorhombic and is much less common. Bannister (1932) did report the presence of marcasite in the Lower Chalk at Dover and states it was overgrown by pyrite. Marcasite is not uncommon in the Cenomanian Ferriby Chalk Formation at Speeton where the colour bands have been lost and the equivalent chalks contain iron sulfide minerals. Both pyrite and marcasite, where they are found, may occur as nodules formed from a multitude of crystals or as single crystals. The marcasite nodules from Speeton are delicate and spiky whereas the typical pyrite nodule from southern England is globular in form ranging from fist-shape to elongated forms that are associated with burrows in the Chalk. In cross section the pyrite nodules may be seen to consist of either a radial crystalline structure based on one or more centres of growth such is typical for southern England, or colonies of crystals as in the nodules from Speeton.

In the Cenomanian Chalk of southern England pyrite nodules and crystals are particularly common in the lower part of sequence where they are usually well preserved having been protected from oxic groundwater by the clay-rich, low permeability marls and marly chalks. Fine-grained iron sulfides – assumed to be pyrite – may occur as (1) framboids, or (2) as small crystals lining the cavity moulds associated with whole or part-aragonite shells (ammonites, gastropods, inoceramid bivalves etc) where the original aragonite has been dissolved or (3) lining the walls of burrows. These have not been dealt with in this study. We have investigated the large, sedimentary bound, pyrite nodules that may vary in form from spherical, ovoidal, cylindrical, branching to irregular shapes – the largest are up to fist size.

In the Cenomanian Chalk of eastern England nodules and crystals of pyrite or marcasite or their oxidised remnants occur in two geological situations. The first are in chalk units that are regionally restricted but are parallel to the stratigraphy (Jeans 1980, fig. 1). Here the development of iron sulfides has been an integral part of the intrinsic diagenesis of the sediment under specific environmental conditions. They are associated with the development of hardgrounds such as the Paradoxica Bed or the Ammonite Beds that are restricted to the condensed sequences on the Midland Shelf. Whether the iron sulfide originally generated was pyrite or marcasite is not known as we have not found any unoxidised sulfide material. The second situation where both pyrite and marcasite have been recorded are in zones of sulphidization that cross-cut the stratigraphy; in this situation the pyrite and marcasite tend to be most frequent in the beds that under normal circumstances are coloured (Text-fig. 6).

The sulfur isotope composition of pyrite ($^{34}S/^{32}S$ ratio, reported versus a standard Vienna Canon Diable Troilite (VCDT) in 'delta notation' – $\delta^{34}S$) may be a useful tool for exploring the timing and nature of precipitation of pyrite within the Cenomanian Chalk of southern England. The precipitation of pyrite requires a source of ferrous iron (reduced, Fe^{2+}) and a source of sulfide. Sulfide is typically produced through microbial sulfate reduction during early diagenesis in the absence of oxygen. During microbial sulfate reduction, the ^{32}S isotope is preferentially reduced, making the $\delta^{34}S$ of the sulfide and thus the resulting pyrite enriched in ^{32}S or 'isotopically light'. If the sulfate is supplied to the locus of microbial reduction in an fully open system, where there is an infinite supply of sulfate, such as fully porous anoxic sediments where sulfate is supplied rapidly to the site of sulfate reduction, then when one mol of sulfate is reduced it is replaced immediately by another mol from the 'infinite reservoir', in this case seawater sulfate. In this case the growing sulfide nodule will display a single δ^{34}S, which is the δ^{34}S of the 'infinite sulfate reservoir' less any sulfur isotope fractionation associated with microbial sulfate reduction. In a partially closed, or closed system where the supply of sulfate is limited or is becoming increasingly limited – such as in the development of a pyrite nodule in less porous sediment – the isotopes of sulfur will distil during microbial sulfate reduction and large sulfur isotope gradients will be observed (Antler *et al*. 2014). In this case, a range of δ^{34}S can be measured across a growing pyrite nodule. If, on the other hand, the sulfide is produced elsewhere and migrates through the wet sediments until it meets and reacts with the iron without the intervention of microbial activity, then, similar to the fully open system case, the δ^{34}S of the pyrite should be constant.

In this paper we present δ^{34}S of pyrite preserved in two iron sulfide nodules from the Cenomanian Chalk of southern England where colour bands are absent, and in seventeen iron sulfide nodules and crystals and one baryte crystal from the Cenomanian Chalk of eastern England where colour bands may be present. We



Text-fig. 2. Distribution of the Chalk and Red Chalk in the UK showing the locations mentioned in the text and in Hu *et al*. (2014) and Jeans *et al*. (2014)

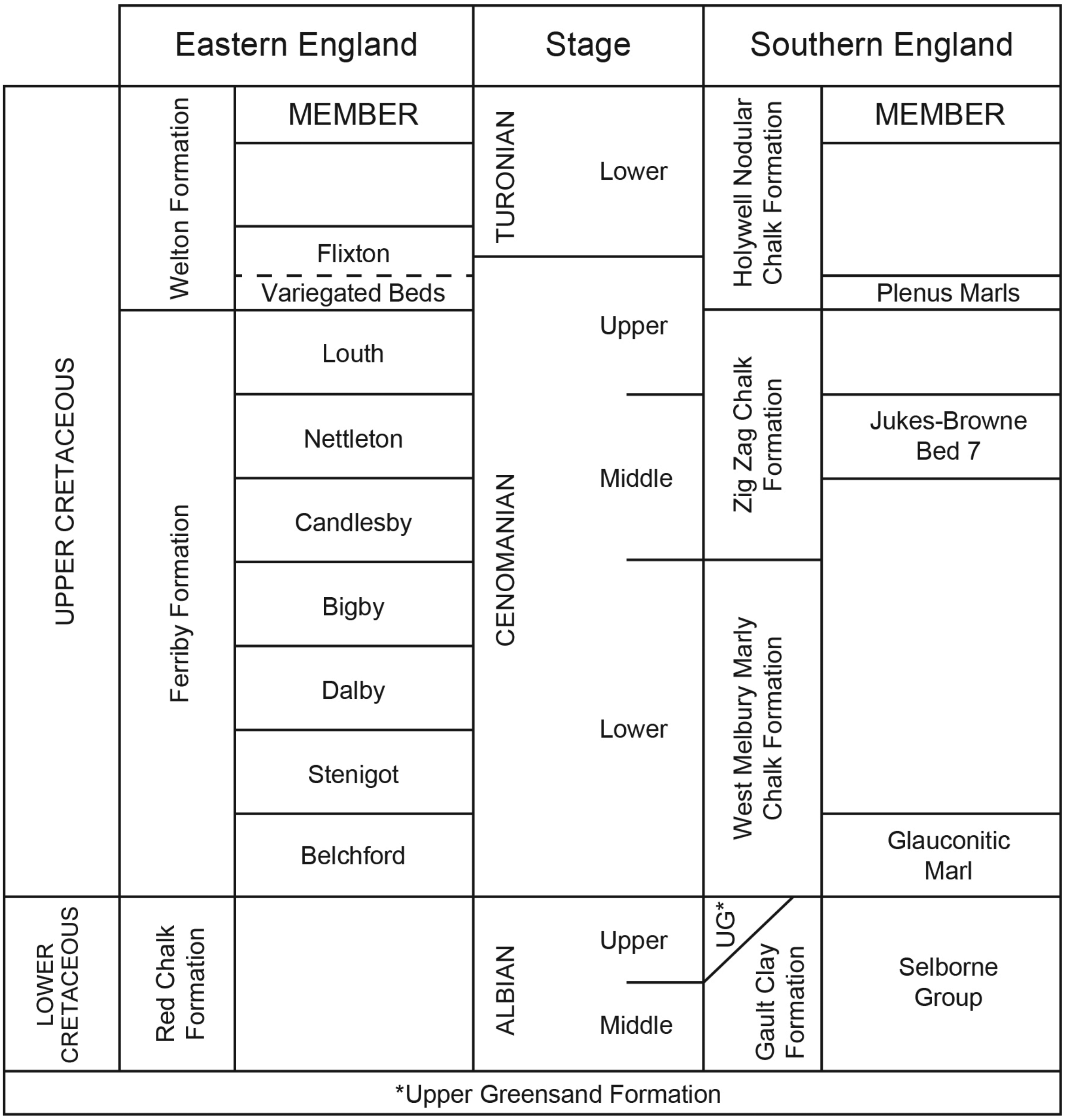
demonstrate that the $\delta^{34}S$ patterns from these two regions are different and this reflects fundamental differences in the origin of the iron sulfide nodules. Using other lines of geological data we discuss (1) the origin and significance of the colour bands in the Chalk and the role played by intrinsic diagenesis, regional tectonism and associated non-intrinsic diagenetic sulfidization in causing their loss in eastern England, and (2) the possibility that these bands reflect enhanced hydrothermal activity or submarine volcanism resulting from the break-up of the oceanic seafloor as North America drifted apart from Europe.

Text-fig. 2 shows the locations mentioned in the text. The general stratigraphical scheme and terms used are in Text-fig. 3.

SAMPLING AND ANALYTICAL METHODS

There were two approaches to sampling:

1. The iron sulfide nodules and crystals were cleaned of their chalk matrix by dissolution in 1molar acetic acid. Nodules that remained coherent after the removal of the supporting chalk matrix and large crystals were sliced in two with a diamond circular saw. Samples for stable isotope analysis were obtained with a



Text-fig. 3. Lithostratigraphical and stratigraphical terms used for eastern and southern England high speed Dremel drill running at ~ 3000 rpm using a fine diamond tipped burr (usually ~ 0.5 mm in diameter). The volume of each sample was generally about 0.25 mm^3. The transect of sampling points in each nodule was chosen to represent its apparent growth with time. In heavily oxidised nodules, small patches of unaltered pyrite were sampled.

2. Nodules that were not coherent once they had been removed from their chalk matrix were disaggregated into their individual crystals or crystal aggregates. These were sieved and separated into 63–125 µm, 125–250 µm, 250–500 µm and >500 µm fractions. Sulfur isotope analysis was restricted to either a single or series of size fractions. Different stages in the development of two delicate stellate marcasite nodules were sampled along their growth axes while still embedded in their chalk matrix. Such nodules were not coherent once the supporting chalk matrix was dissolved. The samples were taken either by drilling or dissection followed by treatment with 1 molar acetic acid to remove traces of chalk, they were crushed prior to analysis.

The authigenic barite crystals in brachiopod T1 were sampled using the Dremel drill in a single section (1 mm thick) chosen from the series into which the specimen had previously been cut.

Pyrite, marcasite and barite were prepared for sulfur isotope analysis through cleaning with a salt solution (to remove sulfate salts) and with deionized water. Microdrilled samples were weighed directly for analysis in the mass spectrometer. Samples were weighed into tin capsules (~300µg of pyrite or marcasite: ~400µg of barite) and an excess of vanadium pentoxide was added. Sulfur isotopes were measured through combustion in a Flash EA coupled by continuous flow to a Delta V Mass spectrometer (Thermo Finnegan). Samples were run in duplicate and bracketed by international standards (NBS 127 δ^{34}S = +20.3‰, IAEA-SO-6 δ^{34}S = -32.3‰). Samples were corrected to a linear regression between the two standards, unless they fell outside the range of +20.3‰ to -32.3‰, in which case they were corrected to the heavier or lighter standard. Sulfur isotope ratios are reported versus the VCDT standard in parts per mil, ‰ using standard delta notation.

Scanning electron microscopy was used to examine the morphology of the pyrite and marcasite crystals from the fine sand fractions. Powder X-ray diffraction was carried out on certain samples to check the identification of pyrite and marcasite.

Stable isotope analysis of bulk samples of Chalk was performed at the Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge. Samples were analysed for oxygen and carbon isotopes (δ^{18}O and δ^{13}C, respectively) of carbonates using either a Micromass Multicarb Sample Preparation System attached to a VG SIRA Mass Spectrometer (prefix S) or a Thermo Electron Kiel Preparation Device attached to a MAT 253 Mass Spectrometer (prefix K). Each run of 30 samples was accompanied by ten reference carbonates and two control samples. The results are reported as delta values with reference to the VPDB and the precision was better than +/–0.06‰ for δ^{13}C and +/–0.06‰ for δ^{18}O.

PYRITE NODULES, CENOMANIAN CHALK, SOUTHERN ENGLAND

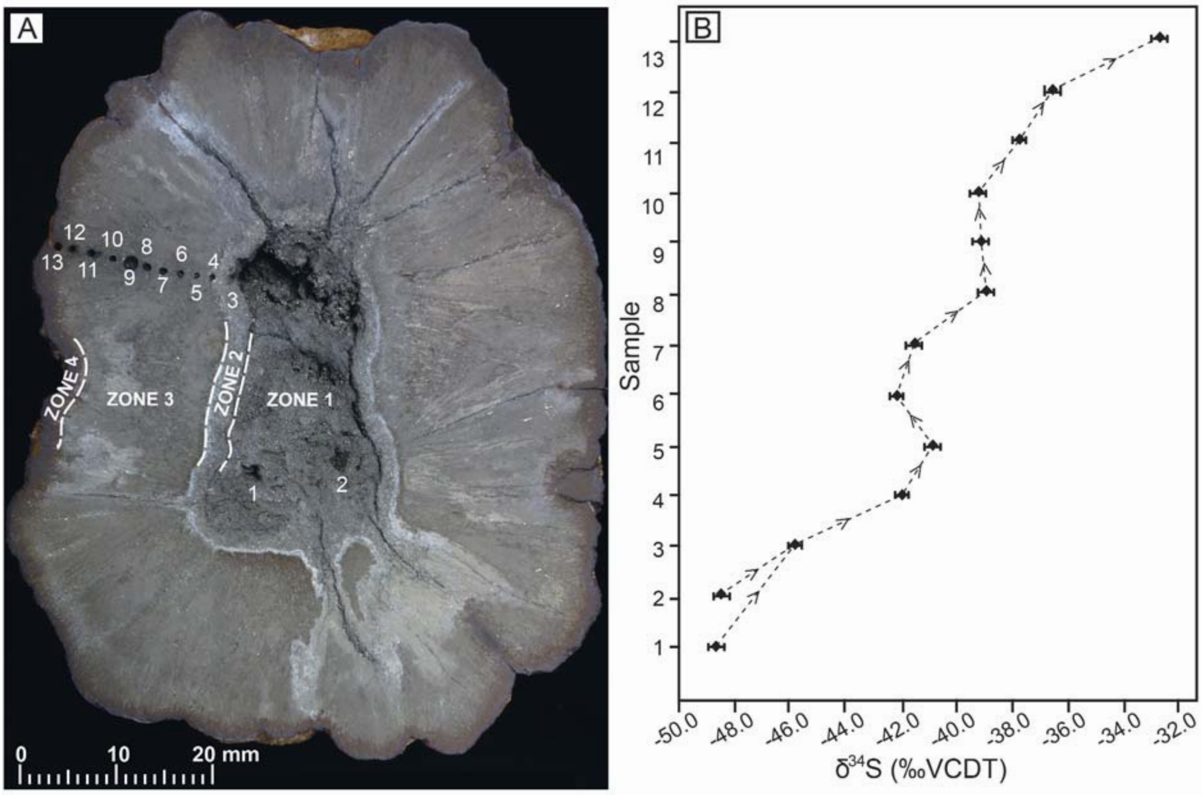
Two pyrite nodules have been investigated, both are from the Cenomanian Chalk at the Southerham Grey Pit, Sussex (Mortimore 2013): one is spheroidal to ovoidal in form and the other is cylindrical with protuberances at one end.

Oval pyrite nodule (Southerham 1)

This pyrite nodule came from the West Melbury Marly Chalk Formation (Text-fig. 3). It is ovoidal in cross-section with a maximum dimension of ~80 mm (Text-fig. 4A). The internal structure shows 4 zones; zone 1 consists of small pyrite crystals intermixed with non-calcareous black pigment, this zone is essentially uncemented and forms the core of the nodule. This is surrounded by zone 2, a thin layer (1-2 mm thick) of fine-grained dense pyrite. Zone 3 (~ 20 mm thick) makes up the bulk of the nodule, it consists of bladed pyrite crystals that are radially arranged and represent a dense growth of pyrite crystal colonies. The outer margin — zone 4 (~ 1 mm thick) that represents the former growing edge replacing the surrounding chalk — is a fine-grained dense pyrite that is slightly limonitised. The forms of the pyrite crystals are visible on the outer surface of the nodule. A total of 14 samples were drilled and the variation in δ^{34}S is shown in Text-fig. 4B and in Table 1. The few samples analysed from within zone 1 show little variation with δ^{34}S averaging around -48.5‰. The radial transect of pyrite analysed from zones 1 to 4 increases in δ^{34}S from -48.1‰ in the core to -32.6‰ near the outer rim (zone 4).

Cylindrical pyrite nodule (Southerham 2)

This sample was collected from Jukes-Brown Bed 7 of the Zig-Zag Chalk Formation. The nodule (Text-fig. 5A) has developed around a ‘worm’ tube of diam-



Text-fig. 4. **A** – Median section showing the sampling transect through an ovoidal pyrite nodule (Southerham 1) from the Middle Cenomanian West Melbury Marly Chalk Formation, Southerham Grey Pit, Sussex. **B** – Pattern of variation in δ^{34}S

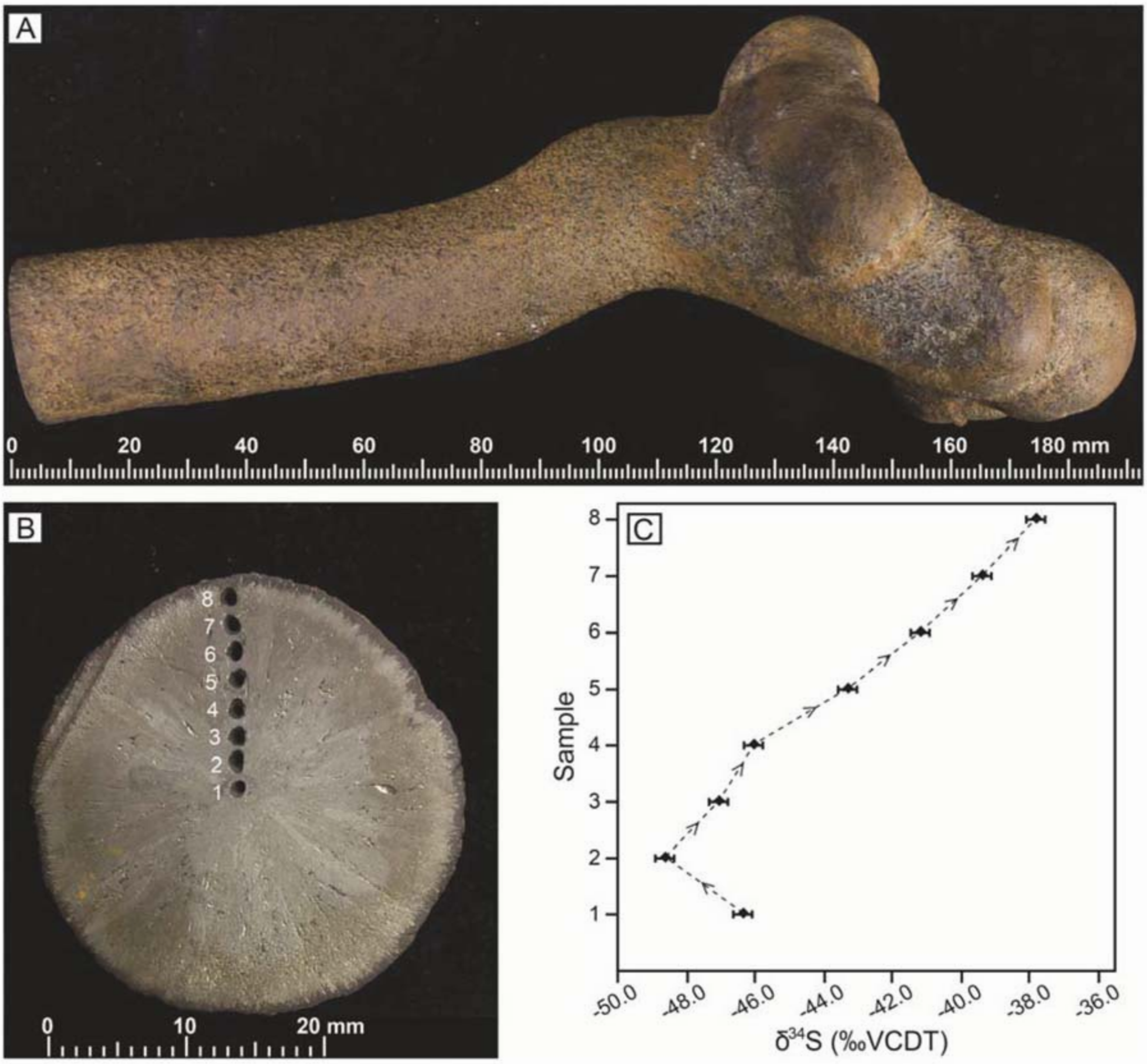
eter ~2 mm. The cylindrical form is almost circular in cross-section (Text-fig. 5B) with a diameter of ~30 mm. It displays only 2 zones, one of bladed pyrite crystals (~ 29 mm thick) that radiate outwards from the pyrite infilling the worm tube and a thin brown limonitised zone (0.5 mm thick) on the outside. The crystal form of the partially limonitised pyrite crystals is visible on the outer surface of the nodule. Eight samples were drilled on a radial transect from the centre to the outer margin. The δ^{34}S is lowest in sample 2 (-48.6‰) and then increases monotonically along the radial transect to -37.9‰ for the outermost sample (Text-fig. 5B and Table 1). The pyrite (sample 1) infilling the worm tube has a value of -46.3‰.

PYRITE, MARCASITE AND BARITE NODULES, CENOMANIAN CHALK, EASTERN ENGLAND

The overall distribution of coloured chalks and weathered and unweathered iron sulfide nodules in the Red Chalk and Ferriby Formations of eastern England is shown in Text-fig. 6. Text-fig. 7 shows the lithostratigraphy of the upper part of the Red Chalk and the Ferriby Formations at Speeton, Yorkshire, and the levels from which samples were analysed. Text-fig. 8 shows the detailed variation in the distribution of coloured and sulphidized chalk in the upper part of the Red Chalk Formation and the Ferriby Formation in the cliffs between Speeton and Buckton, Yorkshire.

Lower zone of iron sulfide nodules, Belchford Member, Ferriby Formation, Speeton

A zone of red coloured chalk is well exposed at the base of Red Cliff, Speeton (Text-fig. 8). Here and in the adjacent intertidal foreshore there is a pale bluish grey zone of variable thickness extending laterally for at least some tens of metres. This replaces the deep red or brownish red colour of the Red Chalk Formation and the overlying Belchford Member of the Ferriby Formation (Text-fig. 9). This bluish-grey zone cuts across the bedding of the red coloured chalks, but in detail it displays a stepwise form, in places the contact is parallel, elsewhere it is cross-cutting. In the near proximity of major E-W joints that cut across the bedding in Red Cliff, the zone of discolouration follows the joints affecting the red chalk on either side following it to higher levels



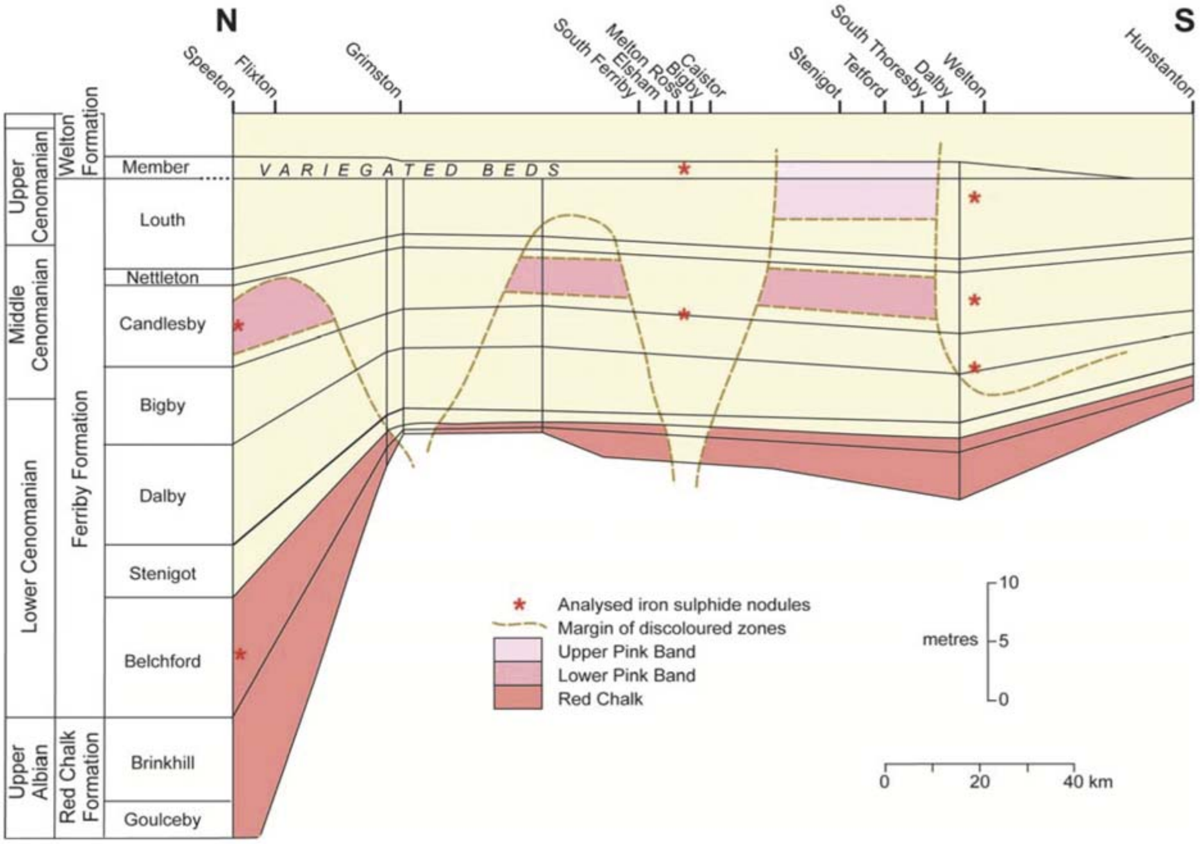
Text-fig. 5. **A** – Cylindrical pyrite nodule associated with a burrow system from the Middle Cenomanian Jukes Browne Bed 7, Zig Zag Chalk Formation, Southeram Grey Pit, Sussex. **B** – Circular cross-section showing the sampling transect. **C** – Pattern of variation in $\delta^{34}S$

where it is no longer recognisable amidst the paler coloured chalks (Jeans *et al*. 2014, text-fig. 22). In contrast to the complete lack of iron sulfide in the red coloured chalk, this zone of discolouration contains many pyrite and marcasite nodules and large separate crystals of pyrite. All the pyrite nodules are of the incoherent type and consist more of colonies of crystals in close proximity rather than a coherent body. The pyrite nodules range in shape from irregular to subspherical. Individual pyrite crystals (Text-fig. 10A, B, C) range up to ~ 20 mm in diameter. The marcasite nodules can be identified by their stellate form (Text-fig. 11A). The distribution of pyrite and marcasite within the bluish grey zone is not random, usually one or the other dominates individual beds of chalk. We have seen no evidence to suggest an order of crystallisation between the pyrite and marcasite such has been observed by Bannister (1932) at Folkestone. Barite crystals have been recorded from the outer margin of this discolouration zone (Hu *et al*. 2012, Text-fig.1). The barite crystals occurred in a vug preserved within the body chamber of a terebratulid brachiopod; these were also analysed for their sulfur isotope composition. Table 2 contains the $\delta^{34}S$ of the samples from the sulfidized zones of discolouration in the Ferriby Formation at Speeton.

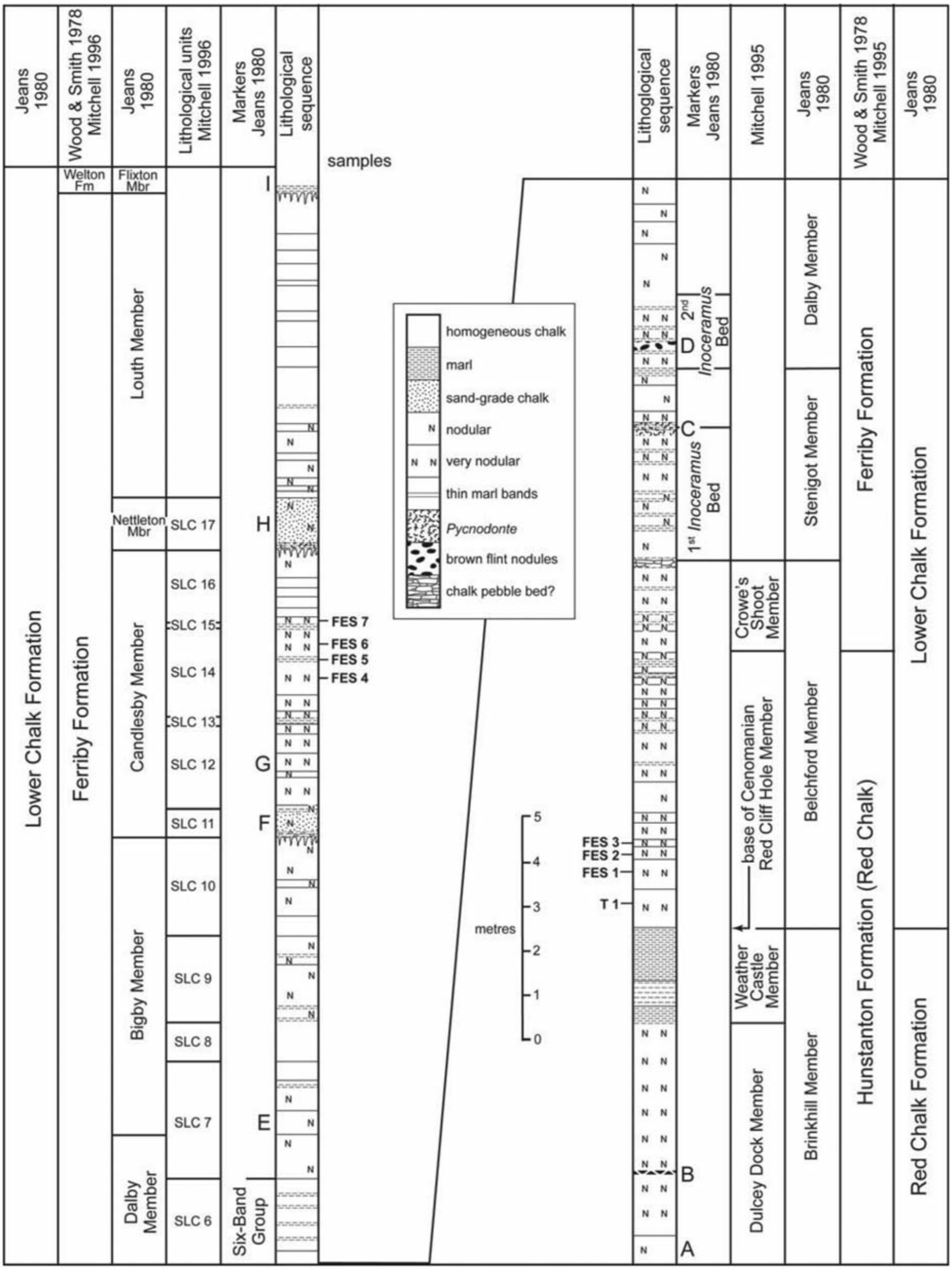
Barite crystals in brachiopod T1: This large specimen of *Concinnithyris subundata* J de C Sowerby was

Sample no.	sample type	Lab. Number	sample number	Mineral Phase	δ^{34}S (‰ VCDT)	stdev	#run
Cenomanian Chalk, southern England							
Southerham. Sussex							
Nodule 1	drilled	CVJST40	3	pyrite	-45.8	0.3	1
	drilled	CVJST41	4	pyrite	-42.0	0.3	1
	drilled	CVJST42	5	pyrite	-40.8	0.3	1
	drilled	CVJST43	6	pyrite	-42.1	0.3	1
	drilled	CVJST44	7	pyrite	-41.5	0.3	1
	drilled	CVJST45	8	pyrite	-38.9	0.3	1
	drilled	CVJST46	9	pyrite	-39.0	0.3	1
	drilled	CVJST47	10	pyrite	-39.2	0.3	1
	drilled	CVJST48	11	pyrite	-37.7	0.3	1
	drilled	CVJST49	12	pyrite	-36.5	0.3	1
	drilled	CVJST50	13	pyrite	-32.6	0.3	1
	drilled	CVJST51	1	pyrite	-48.6	0.3	1
	drilled	CVJST52	2	pyrite	-48.5	0.3	1
Nodule 2	drilled	CVJST53	1	pyrite	-46.3	0.3	1
	drilled	CVJST54	2	pyrite	-48.6	0.3	1
	drilled	CVJST55	3	pyrite	-47.0	0.3	1
	drilled	CVJST56	4	pyrite	-46.0	0.3	1
	drilled	CVJST57	5	pyrite	-43.3	0.3	1
	drilled	CVJST58	6	pyrite	-41.2	0.3	1
	drilled	CVJST59	7	pyrite	-39.4	0.3	1
	drilled	CVJST60	8	pyrite	-37.9	0.3	1

Table 1. Samples, analytical details and δ34S (‰VCDT) of pyrite nodules from the Cenomanian Chalk, southern England

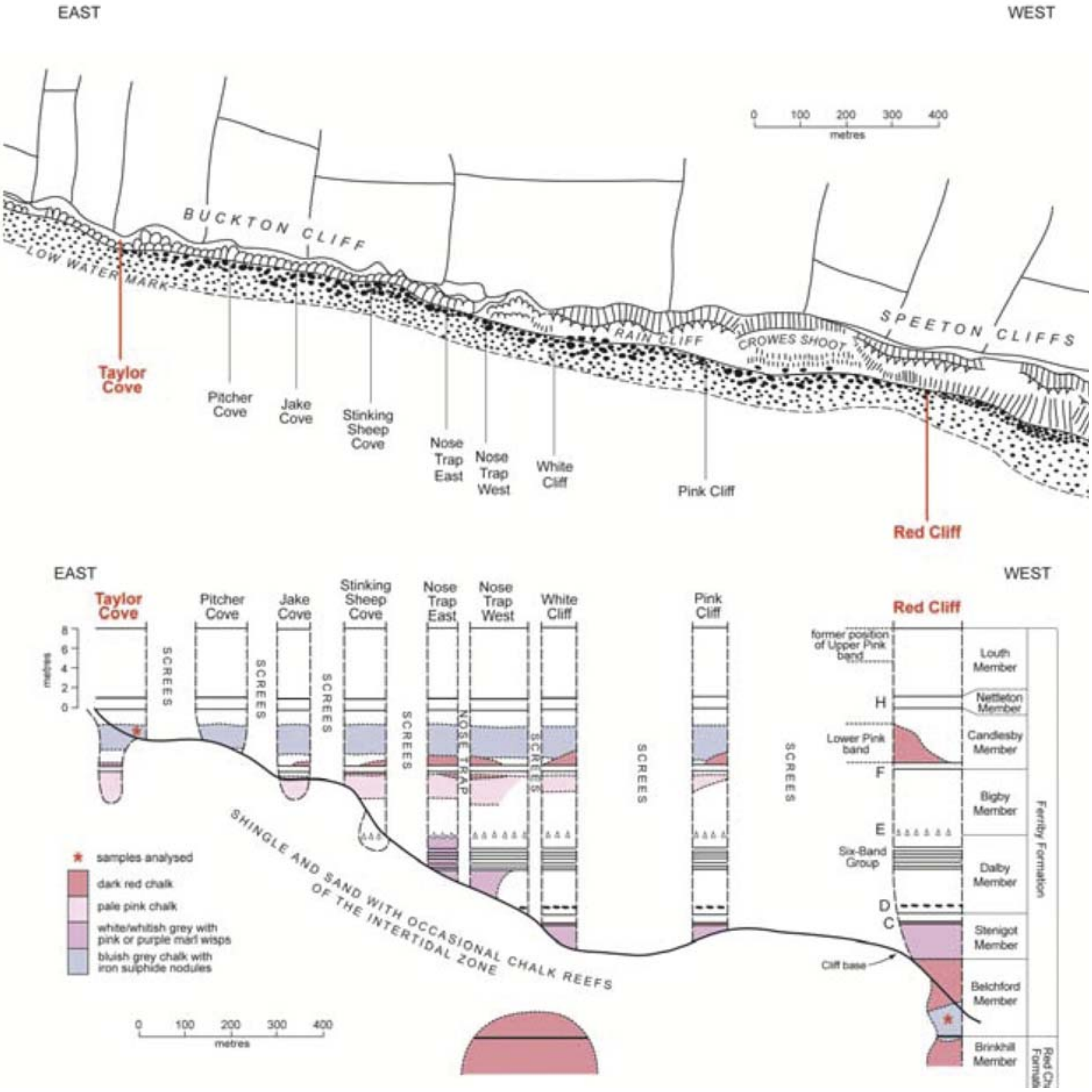


Text-fig. 6. Horizontal section of eastern England showing the overall stratigraphy of the Upper Albian, Cenomanian and Lower Turonian strata and the general distribution of red colouration including the Upper and Lower Pink Bands of Bower and Farmery (1910) and the lower band of red coloured chalk of which the Red Chalk Formation is an integral part. The general location and stratigraphical level of the investigated samples are shown



Text-fig. 7. Lithostratigraphy of the upper part of the Red Chalk Formation and the Ferriby Formation at Speeton, Yorkshire, based upon Jeans (1980, fig. 16). A – *Inoceramus*-rich horizon. B – Breccia-nodule band. C – Band of abundant Pycnodonte. D – Brown flint band. E – Lower *Orbirhynchia* Band. F – Grey Bed. G – Upper *Orbirhynchia* Band. H – Nettleton Stone. I – Variegated Beds. The various schemes of lithological subdivisions used by Mitchell (1995, 1996) and Wood and Smith (1978) are shown. FES1–FES7 and T1 indicate respectively the horizons of the investigated iron sulfide nodules and the barite-containing terebratulid brachiopod collected from near the base of the Belchford Member of the Ferriby Formation at Red Cliff. When serially sectioned the body cavity was found to have been incompletely filled by calcite cement and large euhedral barite crystals (Text-fig. 13). The lower part of the body cavity is filled with red chalk, whereas the chalk matrix in which the brachiopod was embedded is mottled red/bluish grey. Four samples were drilled and these gave $\delta^{34}S$ (barite) ranging from +26.9 to +29.9‰ (Table 2).

Horizon FES1: Four samples were analysed. **Sample 1** was the >500 μm fraction of an incoherent marcasite nodule (Text-fig. 12E) with $\delta^{34}S$ of +7.8‰. **Sample 2** was the >500 μm fraction of an incoherent nodule of pyrite with $\delta^{34}S$ of -24.1‰. Samples 3 and 4 were two examples of large pyrite crystals (up to 12 mm in diameter) that have been cut in half and samples were drilled along their diameters. **Sample 3**, a large pyrite crystal (Text-fig. 10D, 10E) provided eight subsamples. The centre of the crystal has a $\delta^{34}S$ of -34.2‰ and the $\delta^{34}S$ increases toward the outer edges with final ones on the outer rim of -28.4‰ and -29.1‰. **Sample 4**, second large pyrite crystal (Text-fig. 10F, G) shows the same



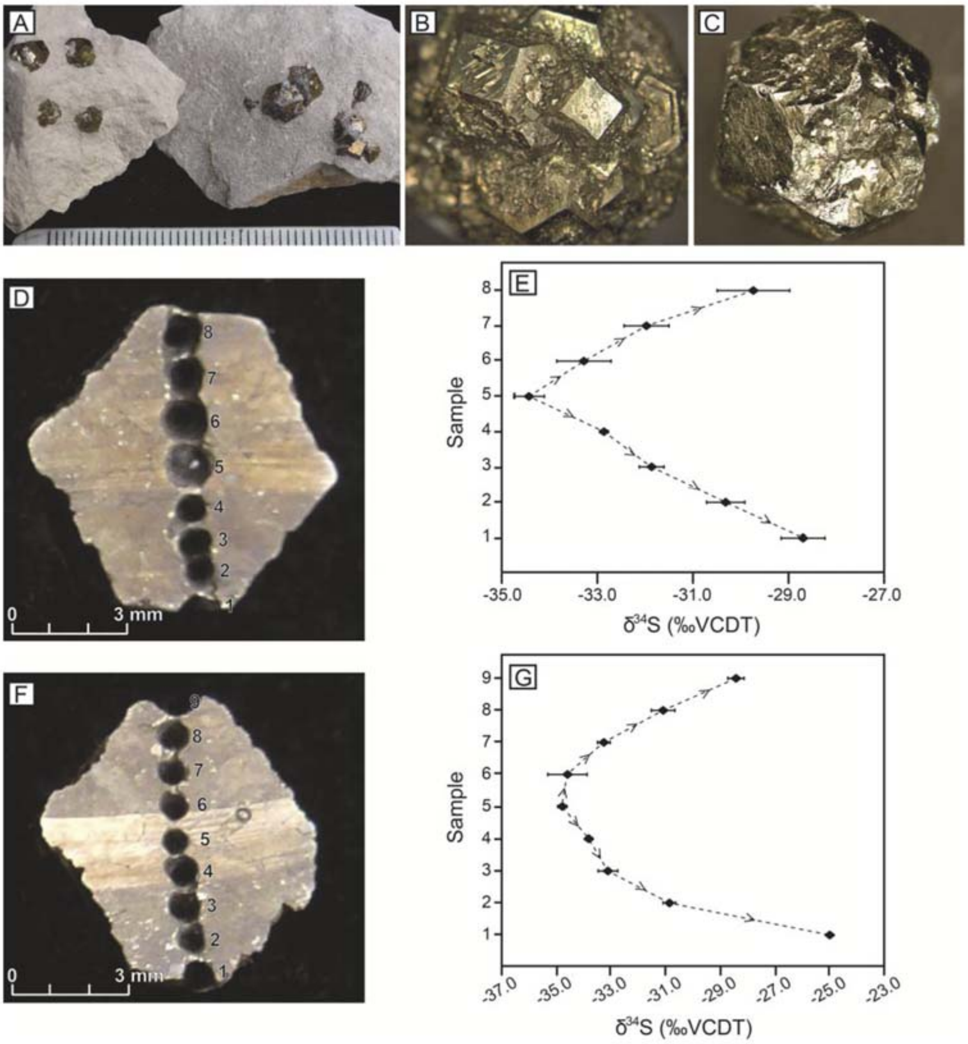
Text-fig. 8. Horizontal sections of the Ferriby Formation and upper part of the Red Chalk Formation at various locations in the cliffs at Speeton and Buckton, Yorkshire. C – Band of abundant *Pycnodonte*. D – Brown Flint Band. E – Lower *Orbirhynchia* Band. F – Grey Bed. H – Nettleton Stone. The distributions are shown of (1) red, pink and purple strata and zones of bluish grey discoloured chalk with iron sulfide crystals and nodules, and (2) the locations and horizons of investigated samples

Text-fig. 9. The Ferriby Formation at Red Cliff, Speeton showing the blue-grey sulfidisation/red colour contact cross-cutting the general direction of bedding in the Belchford Member, Red Cliff, Speeton. Scale, ice axe, 86 cm

pattern with a central δ^{34}S of -34.7‰ and marginal δ^{34}S of -22.2‰ and -25‰.

Horizon FES2: Two samples were investigated. **Sample 1** was the >500 µm fraction from an incoherent marcasite nodule with δ^{34}S of -8.3‰. **Sample 2** was an incoherent marcasite nodule (Text-fig. 11A, B) that was sequentially sampled while still embedded in its chalk matrix from the core of the nodule to the tips of two of its growth spikes. The δ^{34}S ranges from -16.0‰ at the core to -11.0 and -11.3‰ at the tips (Text-fig. 11C).

Horizon FES3: One sample of an incoherent pyrite nodule was examined (Text-fig. 12B). Its 250-500 µm fraction had δ^{34}S of -4.4‰.



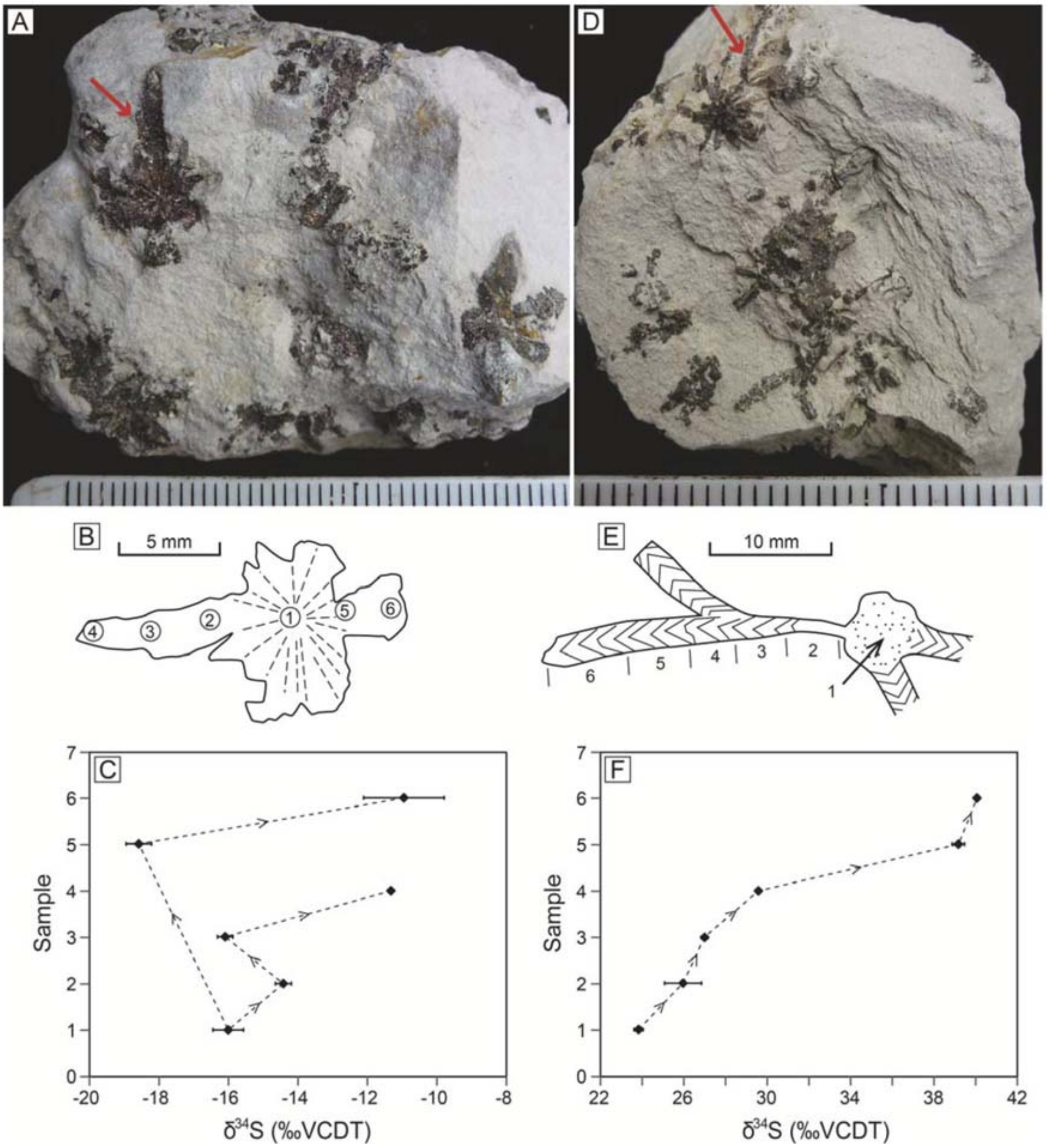
Text-fig. 10. Pyrite crystals in the Belchford Member, Ferriby Formation, Red Cliff, Speeton, Yorkshire. **A** – Clusters of pyrite crystals replacing chalk and nodular chalk. **B** – Large pyrite crystal (~20 mm diameter) displaying a combination of cubic and octahedral faces, FES3. C – Large pyrite crystal (~12 mm diameter) of pyritohedral form, FES3. D – Median section through pyrite crystal 1 (FES3) showing the sampling transect. E – Pattern of variation in δ^{34}S in pyrite crystal 1. F – Median section through pyrite crystal 2 (FES3) showing the sampling transect. G – Pattern of variation in δ^{34}S in pyrite crystal 2

Sample no.	sample type	Lab. Number	sub-sample number	Mineral Phase	d34S (‰ VCDT)	stdev	#run
Cenomanian chalk. Speeton. eastern England							
Upper zone at Speeton (Candlesby Member)							
Horzion FES7							
Sample 1	250-500um	CVJst 007		pyrite.some marcasite	32.5	3.9	4
Horizon FES6							
sample 1	<63um	CVJst 006		pyrite	39.8	0.6	4
			marcasite nodule				
sample 2	dissected	CVJ111ST	1	marcasite	23.8	0.3	2
"	dissected	CVJ116ST	2	marcasite	26.0	1.1	2
"	dissected	CVJ113ST	3	marcasite	27.0	0.2	3
"	dissected	CVJ112ST	4	marcasite	29.6	0.2	2
"	dissected	CVJ114ST	5	marcasite	39.2	0.4	3
"	dissected	CVJ115ST	6	marcasite	40.0	0.1	3
Horizon FES5							
sample1	125-250um	CVJst 001		marcasite	32.9	0.1	3
"	<63um	CVJst 002		marcasite	31.7	0.1	4
Horizon FES4							
sample 1	125-250um	CVJst 003		pyrite	37.7	0.7	4
"	250-500um	CVJst 004		pyrite	39.0	2.2	3
"	63-125um	CVJst 005		pyrite	37.5	0.3	3
Lower zone at Speeton (Belchford Member)							
Horizon FES3							
Sample 1	250-500um	CVJst036		pyrite	-4.4	1.0	3
Horizon FES2							
Sample 1	>500um	CVJst035		marcasite	-8.3	0.2	3
marcasite nodule							
Sample 2	drilled	CVJ105ST	1	marcasite	-16.0	0.6	2
"	drilled	CVJ106ST	2	marcasite	-14.4	0.3	2
"	drilled	CVJ107ST	3	marcasite	-16.1	0.3	2
"	drilled	CVJ108ST	4	marcasite	-11.3	0.1	2
"	drilled	CVJ109ST	5	marcasite	-18.6	0.5	3
"	drilled	CVJ110ST	6	marcasite	-11.0	1.5	2
Horizon FES1							
Sample 1	>500um	CVJst037		marcasite	7.8	1.2	4
Sample 2	>500um	CVJst038		pyrite	-24.1	0.9	3
pyrite crystal 1							
Sample 3	drilled	CVJST102	1	pyrite	-28.7	0.5	2
"	drilled	CVJST101	2	pyrite	-30.3	0.4	2
"	drilled	CVJST100	3	pyrite	-31.9	0.3	2
"	drilled	CVJST99	4	pyrite	-32.9	0.1	2
"	drilled	CVJST86	5	pyrite	-34.4	0.3	2
"	drilled	CVJST87	6	pyrite	-33.3	0.6	2
"	drilled	CVJST88	7	pyrite	-32.0	0.5	2
"	drilled	CVJST89	8	pyrite	-29.7	0.8	2
pyrite crystal 2							
Sample 4	drilled	CVJST94	9	pyrite	-28.4	0.3	1
"	drilled	CVJST93	8	pyrite	-31.1	0.4	2
"	drilled	CVJST92	7	pyrite	-33.3	0.2	2
"	drilled	CVJST91	6	pyrite	-34.6	0.7	2
"	drilled	CVJST90	5	pyrite	-34.8	0.2	2
"	drilled	CVJST95	4	pyrite	-33.8	0.1	2
"	drilled	CVJST96	3	pyrite	-33.1	0.4	2
"	drilled	CVJST97	2	pyrite	-30.9	0.2	2
"	drilled	CVJST98	1	pyrite	-25.0	0.1	2
Brachiopod T1							
T1	drilled	CVJst -8		barite	26.9	0.25	2
"	drilled	CVJst 009 B		barite	28.3	0.48	4
"	drilled	CVJst 010 B		barite	29.9	0.37	4
"	drilled	CVJst 011 B		barite	26.2	0.53	4

Table 2. Samples, analytical details and δ34S (‰VCDT) of iron sulfide and barite nodules from the Cenomanian Chalk, Speeton, eastern England.

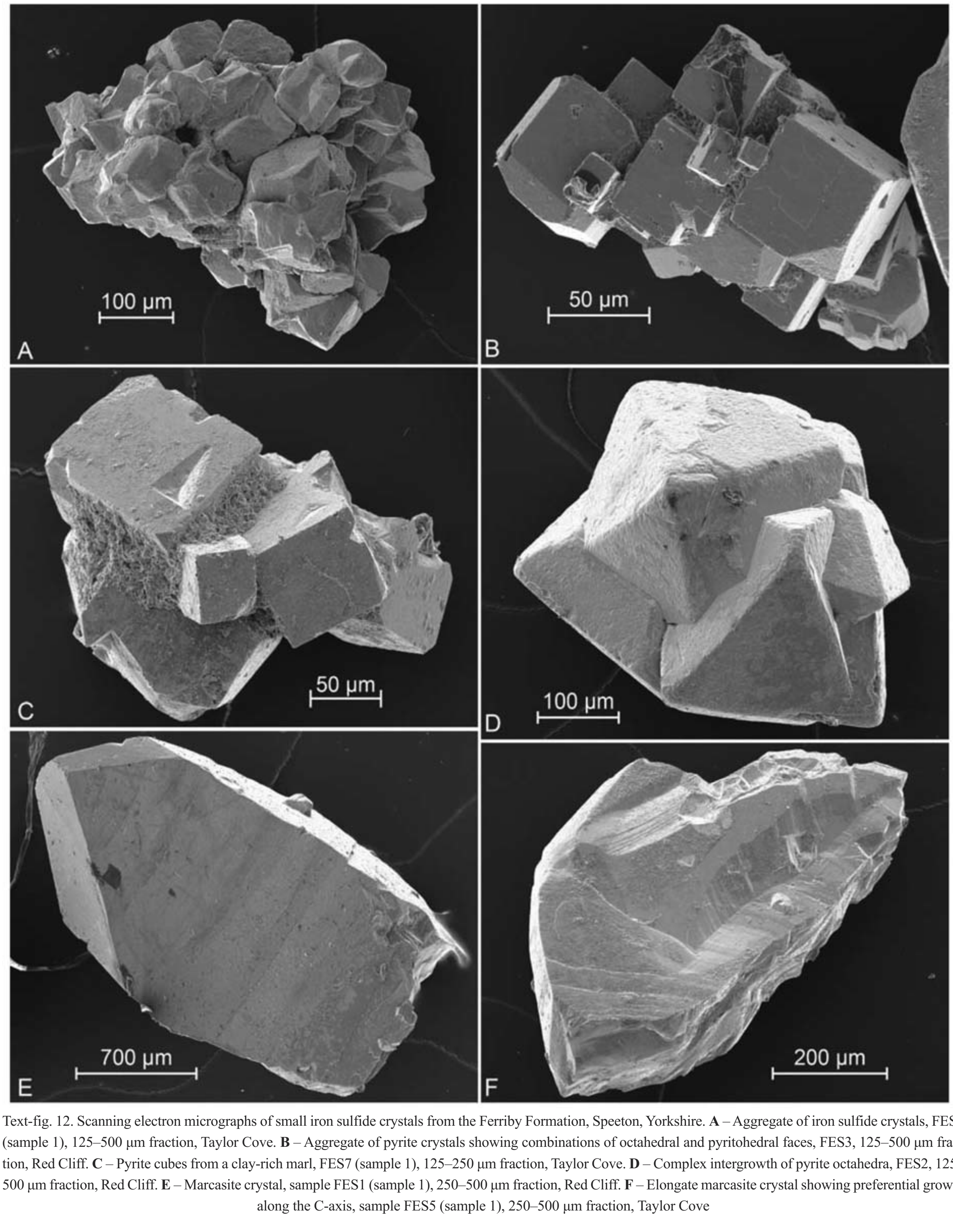
Upper zone of iron sulfide nodules, Candlesby Member, Ferriby Formation, Speeton

High in the Red Cliff section the Lower Pink Band is visible. As it is traced eastwards along the sea cliffs the thickness is reduced to a couple of metres immediately above the Grey Bed at the base of the Candlesby Member of the Ferriby Formation although in places it appears to be completely missing (Text-fig. 8). Where the red colour has been lost the nodular chalks and marls of this interval have a pale bluish grey colour on fresh surface but on weathering they oxidise to a pale ochreous hue. Text-fig. 14 shows the reduced Lower Pink Band at Nose Trap West with the overlying zone of bluish grey/ochreous chalks and marls. Further along the coast at Taylor Cove (Text-fig. 8) the Candlesby Member reaches the cliff base, it lacks any red colouration and contains incoherent nodules of pyrite and marcasite. The marcasite often displays very delicate stellate growth forms (Text-fig. 11D). The primary finding of the sulfur isotope analysis of the pyrite and marcasite sieved from these



Text-fig. 11. Marcasite nodules in the Ferriby Formation, Speeton, Yorkshire. **A** – Stellate nodules replacing chalk. FES2, Belchford Member, Red Cliff, Speeton. Arrow indicates analysed nodule. B – Plan of nodule showing sampling points. C – Pattern of variation in $\delta^{34}S$ in marcasite nodule. D – Delicate stellate nodules replacing marl. Arrow indicates analysed sample. E – Plan of nodule showing the sections analysed. F – Pattern of variation in $\delta^{34}S$ in marcasite nodule nodules is that the δ^{34}S is far more isotopically heavy (higher) than the nodules from the lower zone at Speeton.

Horizon FES4: Three different size fractions from **sample 1** an incoherent pyrite nodule were analysed (Text-fig. 12A). The δ^{34}S of the 250-500 µm, 125-250 µm and 63-125 µm were, respectively, +39.0‰, +37.7‰ and +37.5‰ suggesting the larger grain sizes have a slightly higher δ^{34}S.



Text-fig. 12. Scanning electron micrographs of small iron sulfide crystals from the Ferriby Formation, Speeton, Yorkshire. **A** – Aggregate of iron sulfide crystals, FES4 (sample 1), 125–500 µm fraction, Taylor Cove. **B** – Aggregate of pyrite crystals showing combinations of octahedral and pyritohedral faces, FES3, 125–500 µm fraction, Red Cliff. **C** – Pyrite cubes from a clay-rich marl, FES7 (sample 1), 125–250 µm fraction, Taylor Cove. **D** – Complex intergrowth of pyrite octahedra, FES2, 125–500 µm fraction, Red Cliff. **E** – Marcasite crystal, sample FES1 (sample 1), 250–500 µm fraction, Red Cliff. **F** – Elongate marcasite crystal showing preferential growth along the C-axis, sample FES5 (sample 1), 250–500 µm fraction, Taylor Cove

Text-fig. 13. Section through terebratulid T1 showing the large barite crystals in the body cavity, Belchford Member, Ferriby Formation, Red Cliff, Speeton, Yorkshire

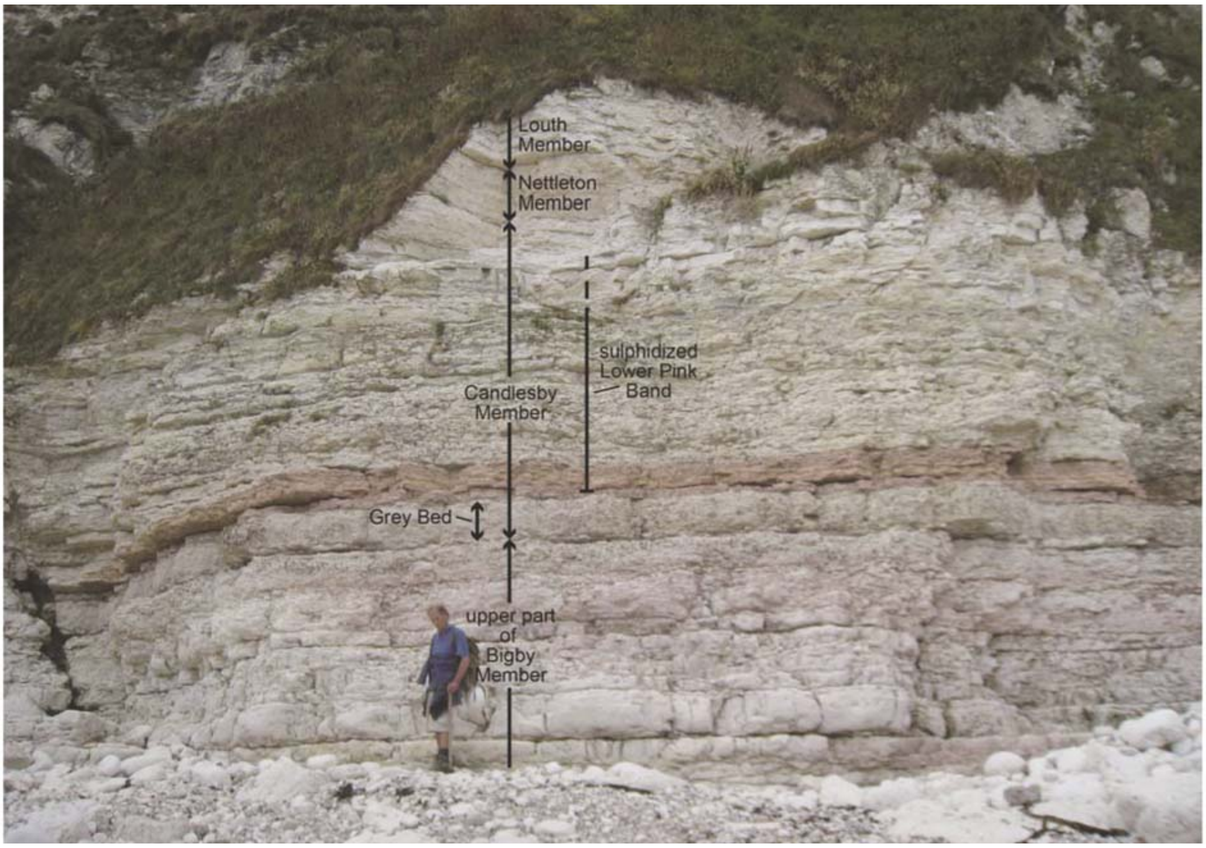
Horizon FES5: Sample 1 was an incoherent marcasite nodule (Text-fig. 12F) with a <63 µm fraction of $\delta^{34}S$ of +31.7‰ and a 125-250 µm $\delta^{34}S$ of +32.9‰.

Horizon FES6: Sample 1 is an incoherent pyrite nodules with a $\delta^{34}S$ for the <63 µm fraction of +39.8‰. Sample 2 is an incoherent marcasite nodule with branching arms with chevron shaped crystals (Text-fig. 11D, 11E) that was sampled from the core to the tip of a long arm. The $\delta^{34}S$ ranges from +23.8‰ at the core to +40.0‰ at the end of the arm (Text-fig. 11F).

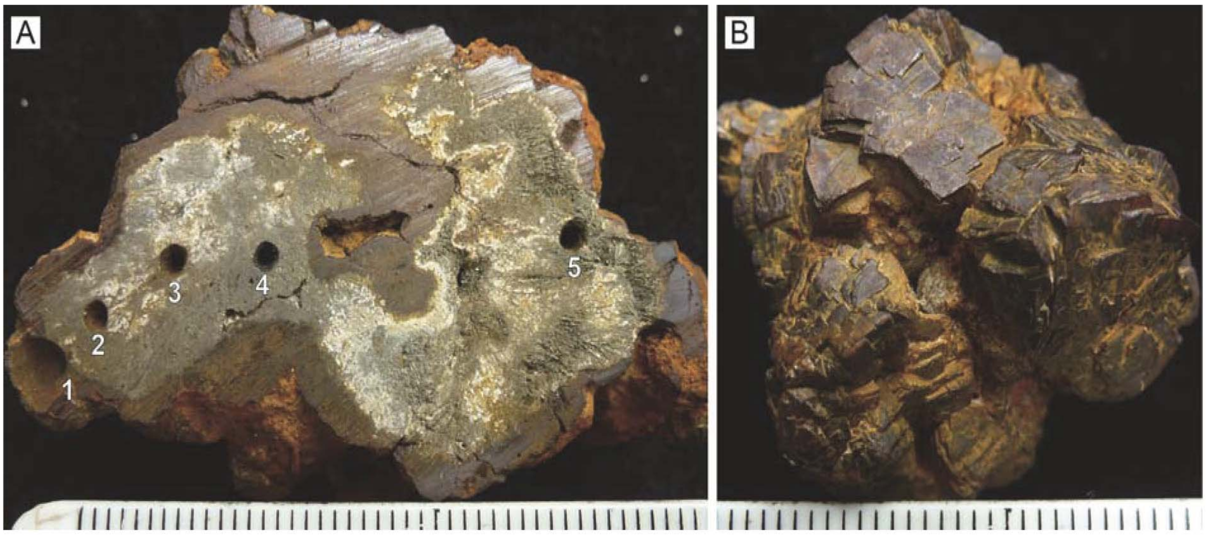
Horizon FES7: Sample 1 is a dominantly pyritic incoherent nodule (Text-fig. 12C) that may contain some marcasite. The $\delta^{34}S$ of the bulk 250-500 µm fraction is +32.5‰.

Iron sulfide nodules, Cenomanian Chalk, Lincolnshire

Text-fig. 6 shows the patchy occurrence of the Lower and Upper Pink Bands between Speeton in the north to Welton in the south, whereas the red band including the Belchford Member and the underlying Red Chalk Formation is continuous except for the region between Elsham and Caistor in north Lincolnshire. Nodules of iron sulfide occur in this cross-cutting zone of discolouration particularly in the strata that represent the position of the Upper Pink Band, the Lower Pink Band, the Belchford Member, and the Red Chalk Formation. These nodules are typically heavily or completely oxidised and only occasionally is unaltered material preserved, usually as localised



Text-fig. 14. Stinking Sheep Cove, Speeton Cliffs, Yorkshire. The pale pink upper part of the Bigby Member and the overlying Candlesby Member of the Ferriby Formation are exposed. The position of the original Lower Pink Band of Bower and Farmery (1910) is shown, only the lowest section immediately above the Grey Bed is preserved, whereas the rest has been sulfidized and is represented by bluish grey marly chalk weathering to an ochreous grey



Text-fig. 15. **A** – Cut surface of partially oxidized pyrite nodule (no. 12) from the top of the Bigby Member of the Ferriby Formation, Bigby, Lincolnshire, showing the sample locations. **B** – Euhedral pyrite crystals on the outer surface of a partially oxidized pyrite (no.17a) from the Bigby or top Dalby Member, Ferriby Formation, Welton, south Lincolnshire

patches. Only pyrite has been found. Limited δ^{34}S was obtained from 5 nodules and are listed in Table 3.

Bigby pyrite nodule 12: This is an irregular shaped nodule with many protuberances. Collected from the very top of the Bigby Member of the Ferriby Formation (Text-fig. 6) in the disused quarry at Bigby (grid ref. TA 059078). The cut surface (Text-fig. 15A) shows a grey inner zone bordered by a dense limonitised outer layer, the outer surface of which displays the crystal form of the pyrite. The grey inner zone displays a white mottling which may be fine-grained gypsum resulting from the localised oxidation of the pyrite and its interaction with the chalk. Five samples were drilled at locations considered to represent growth stages in the development of the nodule. In the inner grey zone δ^{34}S ranges from -10.6‰ to +3.6‰, the sample transect from 1 near the centre of the nodule to 5 (the outer limonitised layer) shows a gradual increase in δ^{34}S from -10.6‰ to +7.6‰.

Melton Ross pyrite nodule 1: This small nodule was found in sample 11 from the Variegated Beds (Black Band/Plenus Marls sequence) in an exploratory excavation

Sample no.	sample type	Lab. Number	sample number	Mineral Phase	δ^{34}S (‰ VCDT)	stdev	#run
Cenomanian chalk, Lincolnshire, eastern England							
Bigby							
Bigby 12	drilled	CVJST61	1	pyrite	7.9	0.3	1
	drilled	CVJST62	2	pyrite	3.6	0.9	2
	drilled	CVJST63	3	pyrite	-5.7	0.8	2
	drilled	CVJST64	4	pyrite	-10.6	0.8	2
	drilled	CVJST65	5	pyrite	-5.7	1.0	2
Melton Ross							
	>250um	CVJST103		pyrite	-29.9	0.3	2
	125-250um	CVJST104		pyrite	-29.2	0.3	2
Welton							
Welton 17a	drilled	CVJST66		pyrite	-19.6	0.7	2
Welton 21e	drilled	CVJST69		pyrite	-24.2	0.7	2
Welton 19	drilled	CVJST70		pyrite	-32.9	1.2	2

Table 3. Samples, analytical details and δ34S (‰VCDT) of iron sulfide nodules from the Cenomanian Chalk, Lincolnshire, eastern England.

Upper Pink Band. Louth Member. Ferrby Chalk Formation

Sample pairs		δ^{18}O‰	δ^{13}C‰		δ^{18}O‰	δ^{13}C‰
Speeton (sulfidized)						
1	marl	−2.80	3.18	chalk	−4.30	2.99
2	marl	−2.09	3.13	chalk	−4.35	2.95
3	marl	−2.68	3.14	chalk	−4.69	2.94
4	marl	−3.39	3.15	chalk	−4.55	2.82
5	marl	−2.69	3.15	chalk	−4.18	2.75
6	marl	−3.33	3.07	chalk	−3.93	2.86
	average marl	−2.83 (stdev.0.48)	3.14 (stdev.0.04)	average chalk	-4.33 (stdev. 0.27)	2.89 (stdev.0.09)
South Thoresby (pink)						
1	marl	−2.41	3.26	chalk	−3.36	3.12
2	marl	−2.33	3.04	chalk	−3.26	3.06
3	marl	−2.33	3.08	chalk	−3.11	3.09
Tetford (anomalous pink)						
1	marl	−2.21	2.48	chalk	−3.37	2.91
2	marl	−3.06	2.68	chalk	−3.09	2.86
	average marl	−2.47 (stdev.0.34)	2.91 (stdev. 0.32)	average chalk	-3.24 (stdev. 0.13)	3.01 (stdev.0.12)

Table 4. Stable isotope values of the calcite in the pressure dissolution marls and adjacent chalks from the Upper Pink Band, Louth Member, Ferriby Chalk Formation, eastern England.

(hole 1) on the floor of the chalk quarry at Melton Ross (Wood *et al*. 1997, p. 334). It occurred in a clay-rich lithology associated with the black organic-rich bands of the Variegated Beds. Whether this is an early nodule related to anoxic conditions developed during the intrinsic diagenesis of the sediment or to the Late Cretaceous or Cenozoic sulphidization is not clear. Two samples gave δ^{34}S of -29 and -30‰.**Welton pyrite nodule 17a:** This nodule was collected loose in a working part of the quarry near Welton Le Marsh (grid ref: TF 451619) in autumn 2013. It came probably from the chalk close to the boundary between the Dalby and Bigby Members of the Ferriby Formation. The nodule has been extensively oxidised with the loss of its core. A thick outer zone of limonitised pyrite is still intact and shows particularly well the form of the pyrite crystals (Text-fig. 15B). A single analysis yielded δ^{34}S of -19.6‰.

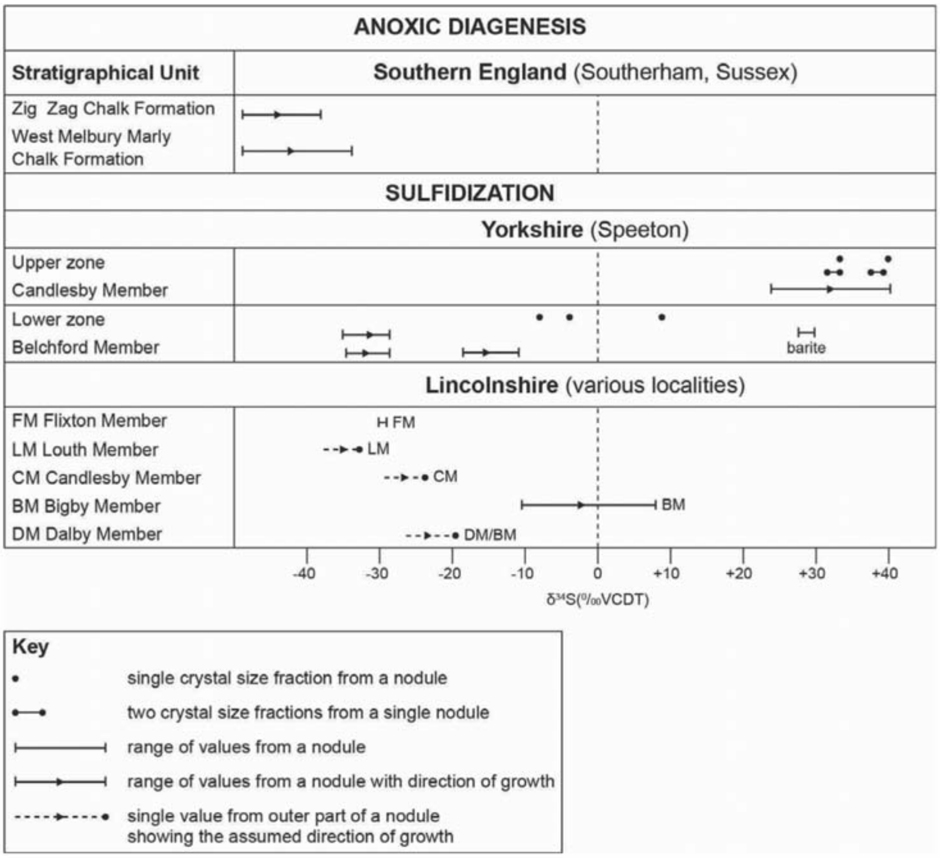
Welton pyrite nodule 21e: This was collected from the Candlesby Member (former position of the Lower Pink Band), Ferriby Formation, in the Welton quarry. Just 16 kilometres to the north at South Thoresby the Candlesby Member displays the deep red and pink colouration of the Lower Pink Band. This is a small nodule, approximately 3 cms in maximum dimension, consisting mainly of a dense limonitised pyrite outer layer. A single sample of this gave a δ^{34}S of -23.4‰.

Welton pyrite nodule 19: Somewhat similar in size and form to the previous nodule (nodule 21e) but from the Louth Member (former position of the Upper Pink Band) at the Welton quarry. A single sample from the outer limonitised pyritic zone had δ^{34}S of -32.0‰.

INTERPRETATION

The range of δ^{34}S displayed by the iron sulfide nodules from southern England and those associated with the zones of sulfidization in eastern England are different although there is some overlap (Text-fig. 16). The two nodules from Southerham, although of different shape and from different horizons in the Cenomanian Chalk display a similar radial growth of pyrite crystals from the core to the outer margin. The oval nodule (Southerham 1) shows an increase in δ^{34}S from -48.6‰ at the core to -32.6‰ at the outer margin. The non-monotonic development of the pyrite in zone 3 (samples 6, 7) could indicate a contribution from new marine pore water with lighter and less evolved δ^{34}S. The cylindrical nodule with protuberances (Southerham 2) shows a similar trend from -48.6 near its centre to -37.9‰ at the outer margin. The slightly heavier value (-46.3‰) of sample 1 from the central worm tube suggests that the pyrite was precipitated here during the early stages in the development of the nodule but after the death of its occupant responsible for initiating nodule development.

The iron sulfide nodules and crystals from the Cenomanian Chalk of eastern England divide into two groups, those from Speeton, and the others from inland Lincolnshire. The Speeton group are typically either represented by single crystals, often of considerable size (up to 20 mm in diameter), or by incoherent nodules that are often made up of colonies of separate crystals or, in the case of marcasite, so delicate that sampling should be done in situ. The Speeton group can be further divided into two subgroups: One is associated with the local zones of discolouration affecting the top most part of the Red Chalk Formation and the lower members (Belchford, Stenigot) of the Ferriby Formation. The other subgroup is associated with the discolouration that affected the Lower Pink Band (Candlesby Member) and this may be part of the main regional confluent zone of discolouration that affected the upper part of the Ferriby Formation over much of eastern England (Text-fig. 6). Although both subgroups are dominated by pyrite with lesser amounts of marcasite, their δ^{34}S are quite different. The lower subgroup with values ranging from -34.2‰ to +7.8‰ overlaps with the values from southern England but extends to much higher δ^{34}S. This subgroup is represented by the large pyrite crystals with values that overlap with the later growth stages of the oval nodule (Southerham 1: Text-fig. 4) from southern England. The other component of the subgroup is the incoherent marcasite and pyrite nodules. Their range of δ^{34}S (-18.6 to 7.8‰) is considerably heavier than those of the large pyrite nodules. A point of caution should be mentioned. Some of our sampling of these incoherent nodules is based upon using different crystal size fractions. The value from each fraction is only the average of a large number of crystals, each possibly with a different δ^{34}S. It is also likely that within each crystal there is a range of δ^{34}S representing its individual growth, which is homogenized during sampling. This also applies, but to a lesser extent, to the marcasite nodule sampled in situ. The arms of the stellate nodule are not simple elongated crystals growing along their C-axis but they are encrusted with small separate crystals often projecting from the arm at various angles (Text-fig. 11A). This problem of sampling scale has been investigated by McConville *et al*. (2000) in an incoherent pyrite nodule from the Jurassic Brent Group in the North Sea using laser microprobe and ion-microprobe techniques. They found a very wide range of δ^{34}S from -10‰ to +50‰ with mean values, depending on methods, of +25.1 ± 13.5‰ (ion microprobe), +21.6 ± 13.3‰ (laser microprobe) and +24.4 ± 12.5‰ (bulk sample).



Text-fig. 16. Stratigraphical and regional distribution of δ^{34}S measured in the various iron sulfide nodules from the Cenomanian chalks investigated in eastern and southern England

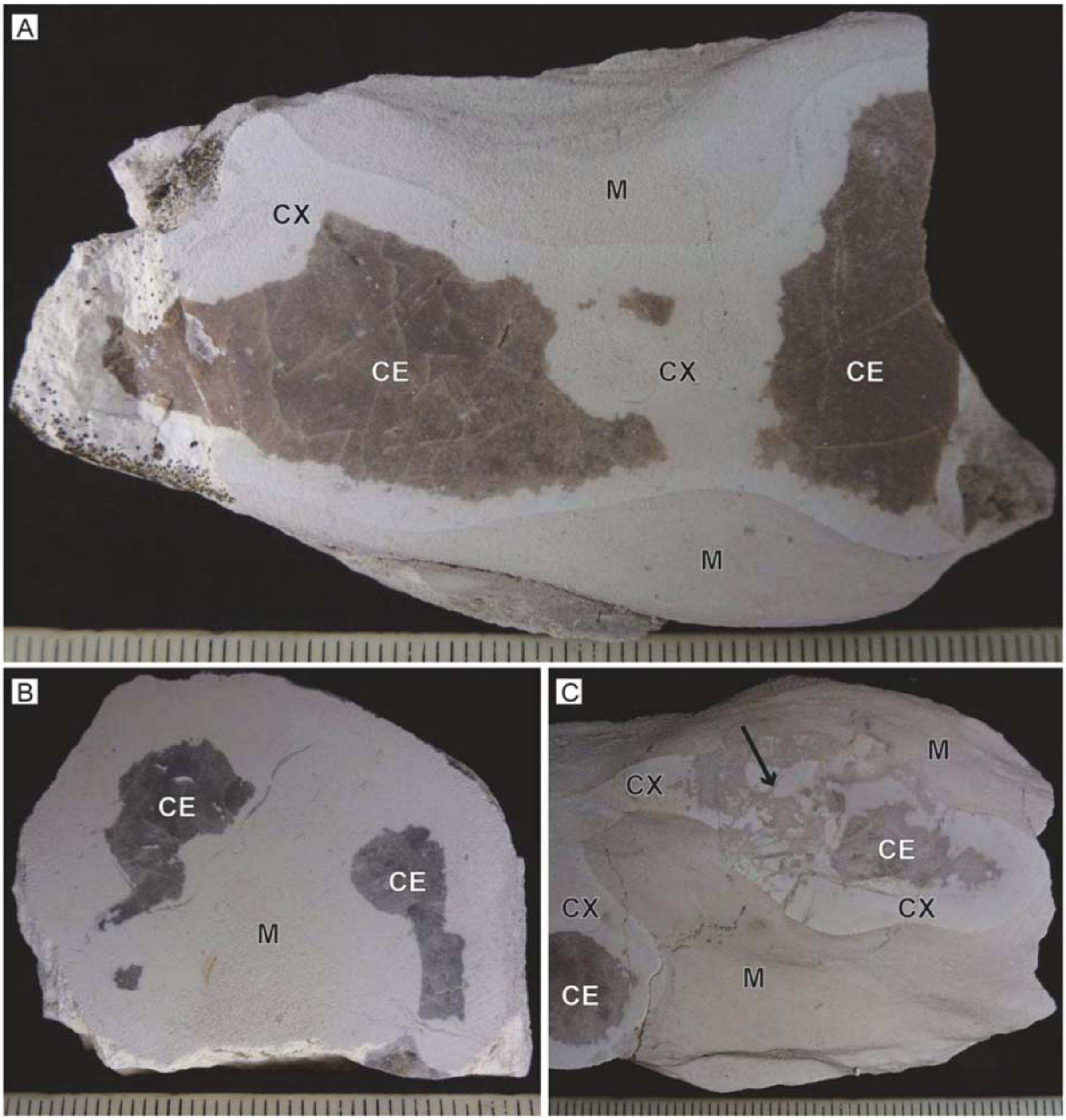
This suggests crystal scaling and growth at different times in the evolution of the sulfate content/history of the pore solutions. In our investigation of these incoherent nodules where specific size fractions have been analysed we have found that if more than one fraction has been analysed from a particular sample, the larger size fractions always have heavier $\delta^{34}S$ indicating perhaps that the larger crystals represent the more successful members of the crystal colony that maintained growth into the later stages of the isotopically-evolving sulfate-containing porefluids.

The second subgroup at Speeton consists of incoherent nodules with a range of $\delta^{34}S$ for the different size fractions from both pyrite and marcasite nodules, ranging between +31.7 and +39.0‰. The same sampling limitations apply to these as to the earlier group (McConville *et al*. 2000). These $\delta^{34}S$ probably represent the mean values of populations with a considerable range of $\delta^{34}S$ with some much higher and lower than the mean, perhaps from +51 to +26‰ if comparison is made with the results of McConville *et al*. (2000) from the North Sea. The actual and inferred range of $\delta^{34}S$ is outside the measured mean ranges from the incoherent nodules in the first subgroup at Speeton. This is confirmed by the results obtained from sampling the marcasite nodule (sample 2, horizon FES6) *in situ* where we found that the $\delta^{34}S$ ranges from +23.8 to +40.0‰. With even smaller and more restricted samples this range is likely to be extended closer to that reported by McConville *et al.* (2000).

Evidence of oxic and suboxic zones of diagenesis

The sulfur isotope record in the large pyrite nodules from the Chalk in southern England requires that anoxic conditions and sulfate reducing bacteria were active during the early stages of intrinsic diagenesis. It seems that no geochemical or mineralogical evidence is preserved of the chalk sediment's passage through the zones of oxic and suboxic diagenesis. One reason for this may be the lack of any early cementation that was involved or associated with the reduction of nitrate, manganese oxides or the postulated iron hydroxides during the oxic and suboxic phases. Evidence of this transitory phase of oxic and suboxic diagenesis is sometimes preserved in flints, although the traditional interpretation is that the flints of the Chalk formed within and are genetically related to the anoxic zone of diagenesis (Clayton 1986), rather than the oxic and suboxic zones. Indeed, many flints may have developed only within the anoxic zone but there is clear evidence that some started their development within the oxic and suboxic zones. Flints are exceptionally rare in the Cenomanian Chalk of England. A few small grey flints occur in Dorset at Ballard Cliff and White Nothe (Jeans 1978, fig. 5). A single flint band is known from the Cenomanian Chalk of eastern England, this is the Brown Flint Band described by Jeans (1978, p. 117) from the Lower Cenomanian part (lowest part of the Dalby Member) of the Ferriby Formation at Speeton. It is of particular interest. The flint nodules are small and consist typically of a dense brown translucent core (Text-fig. 17A) of α-quartz possibly with a trace of opal-A – the bioclasts have been completely replaced – and euhedral feldspar crystals are embedded in the core (Jeans 1978, fig. 14d). The cortex is thick, white and sharply defined from the core and the chalk matrix. At Red Cliff (Text-fig. 8) the Brown Flint Band is within a 'white' nodular chalk some two metres above the top of the coloured Belchford Member. Its brown cores are interpreted as having preserved the ferric hydroxide of the early chalk sediment from the effects of the anoxic zone of microbial diagenesis. When this band is traced eastwards the colour of the flint cores and the chalk matrix changes. At Pink Cliff (Text-fig. 8) the brown colour may be present or it may be greyish brown (Text-fig. 17C) whereas in the western end of Nose Trap West (Text-fig. 8) the cores are grey (Text-fig. 17B) and the surrounding nodular chalk, although maintaining the general arrangement of the bedding, displays slickensides, minor tectonic disturbances and ochreous stains as well as containing heavily or completely oxidised small iron sulfide crystals. This association of colour change in the flint core and the presence of iron sulfide minerals in the chalk matrix hints that both are the result of the same process that is responsible for the main discolouration zones at Speeton. In this case, the diagenetic solutions penetrated not only the Chalk but the flints as well. The flint cores, now with very little porosity, must have been in a different physical state and were much more permeable. Text-fig. 17C shows a partially fractured grey brown flint from Pink Cliff affected both by sulfidization and by associated tectonic movement related possibly to uneven compaction within a nodular chalk following the loss of overpressure associated with the Flamborough Head Fault system (Jeans *et al*. 2014).

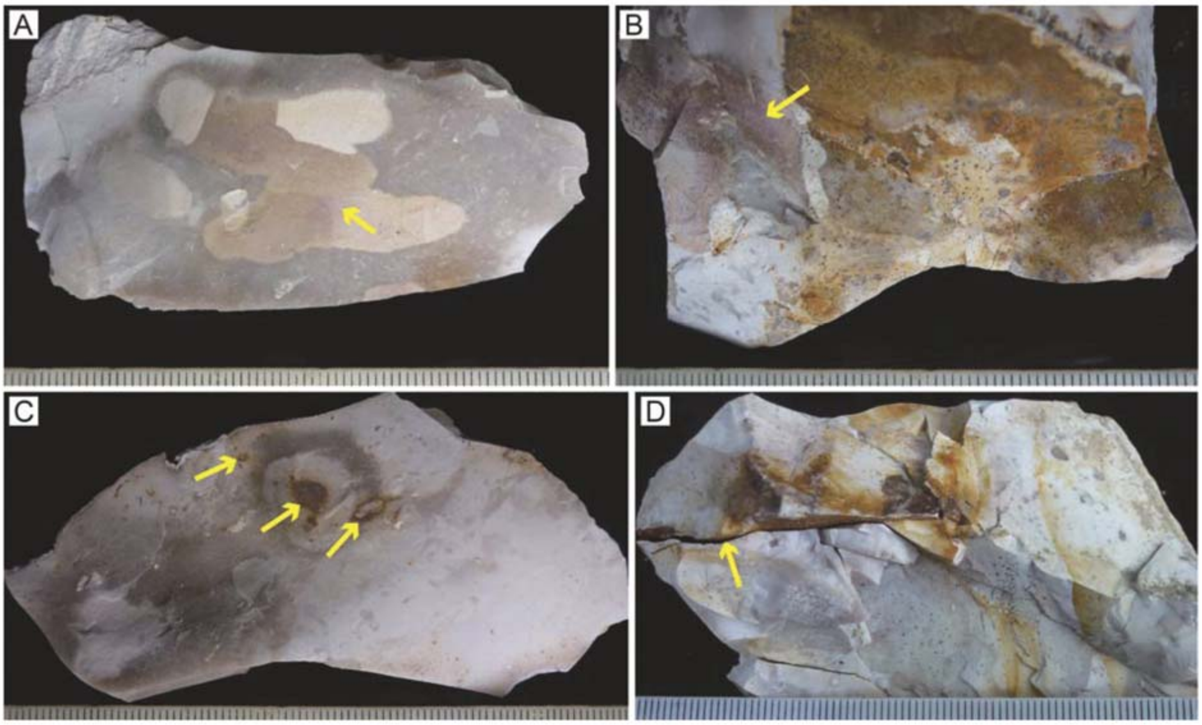
Certain flints from uncoloured Turonian chalks may contain silicified red, reddish brown or pink sediment preserved by silicification from the anoxic stage of Chalk diagenesis. Their chalk matrix we consider to have lost its ferric hydroxide (praecursor of the red pigment) by microbial iron reduction either during intrinsic or non-intrinsic diagenesis (see earlier). The most spectacular are the red flints from the Turonian of Helgoland. They were first illustrated in colour by Schmid and Spaeth (1991, pp. 100–103) and they occur in a white chalk matrix. The Helgoland flint in Text-fig. 18 associated with a white chalk matrix demonstrates clearly that silicification was already well advanced in the oxic/suboxic zone preserving red coloured sediment before the development of the outer black zone of the core in the anoxic zone. Less spectacular but of equal interest is the Ferruginous Flint Band at Melton Ross in Lincolnshire (Text-fig. 2) situated on or close to the tectonic line along which hydrocarbon-rich sulfate-containing solutions are postulated to have entered the Chalk during reservoir collapse (Jeans *et al.* 2014). Within this semi-continuous nodular layer of flint, some of the silicified burrow fills are pinkish, and in other parts there are rusty spots and traces reflecting the oxidised remnants of iron sulfide minerals (Text-fig. 19A–D). Fractures within the flint are rust stained and in places they are filled with the oxidised remains of iron sulfide (Text-fig. 19D). The history of this



Text-fig. 17. Brown Flint Band, Stenigot Member, Ferriby Formation, Speeton, Yorkshire. **A** – Brown core facies from Red Cliff. CE— core, CX— cortex, M— chalk or marly chalk matrix. B – Grey core facies from Nose Trap West lacking an obvious cortex differentiated from the matrix. **C** – grey/brown core facies with a well defined cortex displaying fragmentation (arrow)

Text-fig. 18. Red flint from the Turonian Chalk of Helgoland. The well-defined red zone in the centre of the core is surrounded by black flint, and then by a white cortex

particular flint band reflects the interaction between the initial development of a flint nodule within or just below the oxic/suboxic zone and its continued development in the anoxic zone, then to be fractured and penetrated by the fluids responsible for regional iron-sulfide mineral formation that have been forced out of the North Sea Basin or some other source along the Caistor basement fault sometime during Late Cretaceous or Cenozoic times (Jeans *et al.* 2014, text-fig. 21). Other examples of pink/violet colour flints have been recorded in Turonian Chalk. They are known to occur in the Bridgewick Beds (Lewes Chalk: Late Middle to Early Upper Turonian in age) in southern England as well as in the Turonian Chalk at Criel-Plage, Normandy, in France (Rory Mortimore, personal communication).

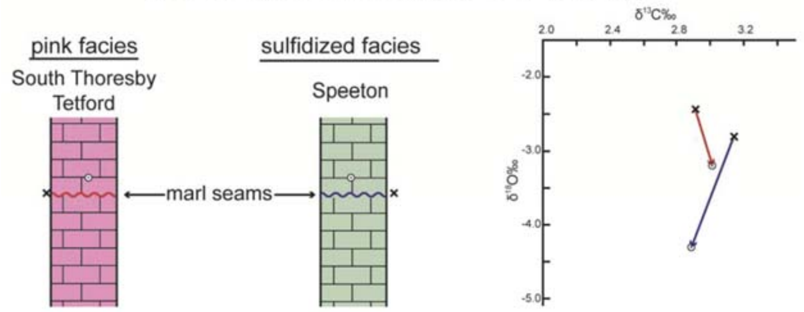


Text-fig. 19. The Ferruginous Flint Band, Lower Turonian, Welton Formation, Melton Ross, Lincolnshire. A – Pink and buff coloured silicified burrow-fills in the grey core. B – Pink-tinged partially silicified burrow fills in the cortex. C – Small oxidised pyrite nodules with alteration zones in the flint body. D – Fractures in the flint filled by oxidized pyrite

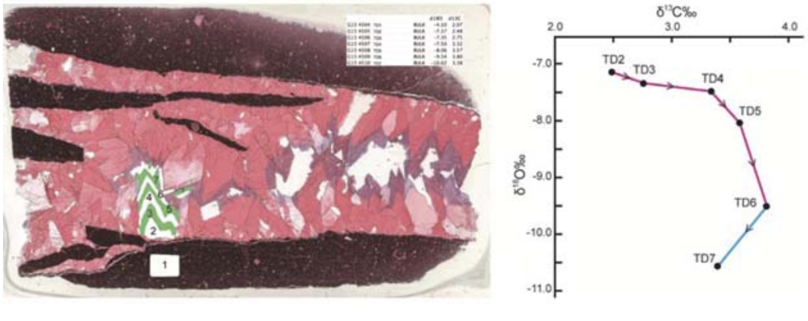
Cross-cutting sulfidization and hardening of the Chalk

Jeans *et al.* (2014) have suggested that the regional hardening of the Ferriby Chalk of eastern England and the zones of cross-cutting sulfidization were coeval and resulted from processes associated with the activities of the three basement faults – Flamborough Head Fault Zone, Caistor Fault, Wash Line of Jeans (1980) – during the Late Cretaceous or the Cenozoic. In this work, it was suggested that movement on these faults was responsible for damaging the seals in the overpressured Upper Cenomanian and Lower Turonian chalks and this caused a marked increase in grain pressure, extensive pressure dissolution of calcite grains, and the development of pressure dissolution features (stylolites, marl wisps and secondary marl seams). The dissolved $CaCO_3$ was precipitated in the surrounding chalk as a late-stage calcite cement and as fracture fills. At the same time and perhaps the cause of the tectonic activity was the penetration of allochthonous fluids, possibly under high pressure, along these basement faults across the Red Chalk Formation and into the Cenomanian and Turonian chalk where they flooded the poorly or unlithified parts of the sediment. These fluids dissolved any reducible iron hydroxides or oxides and this resulted in the precipitation of iron sulfide nodules and crystals. The original evidence supporting this hypothesis came from systematic differences in the carbon and oxygen isotope composition of the bulk calcite in pressure dissolution marl seams and the adjacent beds of chalk from the Louth Chalk Member at Speeton (Jeans *et al.* 2012, table 6; Hu *et al.* 2014, table 4). Here the Upper Pink Band has been sulfidized and the chalk contains the oxidised remains of what we assume to have been iron sulfide. The systematically lighter values of $\delta^{18}O$ and $\delta^{13}C$ for the chalk beds was related to (1) the enhanced temperature at which cementation took place, and (2) the selective pressure dissolution of the calcite of the finest coccolith debris with its low $\delta^{13}C$ relative to the other bioclastic components of the Chalk (Jeans *et al*. 1991) and the subsequent incorporation of this isotopically lower bicarbonate in the new cement of the surrounding chalk. However new evidence suggests that although this is likely to be an influence in affecting the $\delta^{13}C$ of the new cement, it is not the underlying cause of the difference. Table 4 shows the $\delta^{18}O$ and δC^{13} values of the calcite in a number of

A. Marl seams, Louth Member, Ferriby Formation



B. Calcite vein, Flamborough Chalk, Selwicks Bay, Yorkshire



Text-fig. 20. **A** – Comparison of the average $\delta^{18}O$ and $\delta^{13}C$ values of the bulk calcite from the pressure dissolution marls and the adjacent chalk from the Upper Pink Band (Louth Member) at South Thoresby and Tetford with the sulfidized chalk at the same horizon in the Louth Member at Speeton. **B**. 1 – Stained thin section of a calcite vein from the Flamborough Head Chalk Formation at Selwicks Bay, Yorkshire, sampled for stable isotope analysis. This shows the non-ferroan nature of the main body of crystal growth but with a final phase of ferroan calcite. The growth stages and sampling zones in the calcite crystal analysed for stable isotope values are shown. 2 – Cross-plot of the $\delta^{18}O$ and $\delta^{13}C$ values shows that the calcite crystal initially grew with increasing $\delta^{13}C$ values (suboxic pattern of Hu *et al*. 2012) and then in its final stages these values started to decrease in the ferruginous zone (anoxic pattern of Hu *et al*. 2012) pressure solution marl seams and their adjacent chalk from the Upper Pink Band of the Louth Chalk Member at (a) Speeton where it has lost its colour as a result of sulfidization, and (b) at South Thoresby and Tetford where the colour is generally preserved with little or no evidence of sulfidization. In the Upper Pink Band at South Thoresby there is either no difference between the $\delta^{13}C$ of the bulk calcite of the chalks and the marl seams or the chalk has a heavier $\delta^{13}C$. At Tetford the colouration of the Upper Pink Band is atypical and this could reflect partial sulfidization; here the $\delta^{13}C$ values are variable, for one pair of samples there is no difference, for the other the chalk has a lighter $\delta^{13}C$ more akin to those characteristic of Speeton. The chalks in all five sample pairs from south Lincolnshire, like those from Speeton, have lighter $\delta^{18}O$ than the marls. At Speeton these differences are more pronounced. Text-fig. 20A summarises these relationships.

These differences are now interpreted as reflecting the two cementation series recognised by Hu *et al.* (2012), the suboxic series with its increasing $\delta^{13}C$ with time being associated with the Upper Pink Band. In south Lincolnshire this style of cementation continued during pressure dissolution at South Thoresby, whereas at Speeton where the sulfidization fluids had destroyed the Upper Pink Band and had introduced anoxic conditions the original suboxic style of cementation changed to the anoxic series. Intermediate between these situations was Tetford where both suboxic and anoxic cementation may have been involved during this late stage cementation. Further evidence of the close association between the late hardening of the chalk and the development of the sulfidization zones and the change from suboxic to anoxic cementation comes from a recent unpublished investigation by J.A.D. Dickson on a calcite vein from the Flamborough Chalk Formation at Selwicks Bay from within the Flamborough Head Fault Zone. This is illustrated in Text-fig. 20B. Staining shows that there is a late ferroan-rich phase of crystal growth. Stable isotope analysis indicates that the main part of the crystal growth took place with a steady increase in $\delta^{13}C$ from 2.48‰ to 3.80‰ until the ferroan-rich zone is reached when this values drops to 3.38‰ reflecting the change in cementation from suboxic to anoxic. The $\delta^{18}O$ of the calcite decreased gradually from -7.17‰ to -10.62‰, probably indicating the increasing temperature of precipitation.

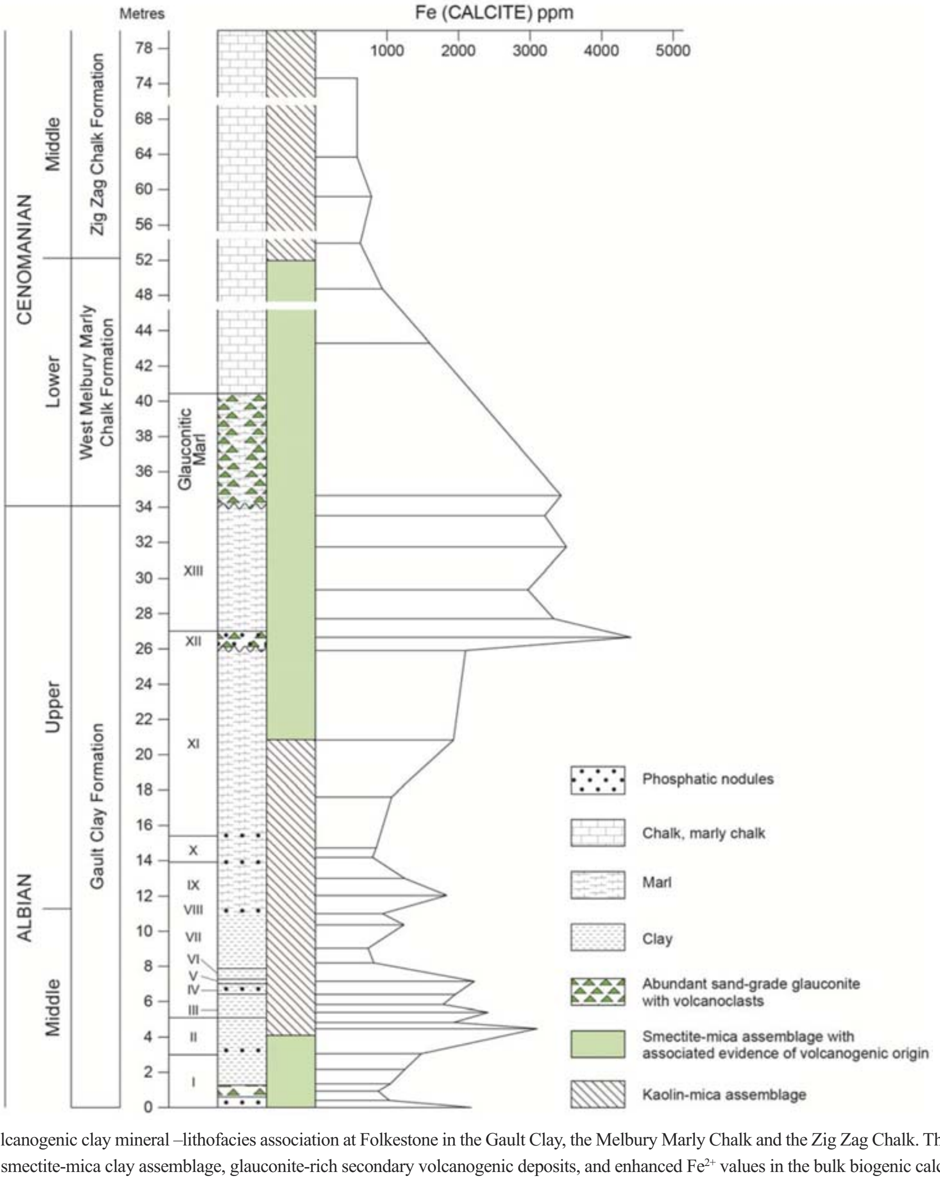
Origin and nature of allocthonous sulfidizing fluids

Regional evidence (Text-fig. 6; Jeans *et al.* 2014) indicates that these fluids entered the Cenomanian chalk through the three basement faults – Flamborough Head Fault Zone, Caistor Fault, and the postulated Wash Line of Jeans (1980). Whether this took place as a single regional event—perhaps part of the break out of overpressured fluids from the adjacent North Sea Basin during regional tectonic activity – or as more restricted events related to localised movement along individual faults is not clear. The regional and stratigraphical patterns of $\delta^{34}S$ displayed by the iron sulfide nodules in eastern England suggests that regionally fluids were of different origin, or at least in different stages in their sulfur isotopic evolution. Those affecting the chalk at Speeton seem to represent two main phases of invasion: one associated with the development of iron sulfide nodules in the lower part of the sequence (Belchford and Stenigot Members) with $\delta^{34}S$ ranging from -34.2 to +29.9‰, the other in the Candlesby Member characterised by much heavier $\delta^{34}S$ giving rise to nodules with $\delta^{34}S$ of +23.8 to +40.0‰. In Lincolnshire, the limited data ($\delta^{34}S$ from -32.0 to +7.6‰) are closer to the nodules from the lower part of the Cenomanian chalk at Speeton but without any obvious stratigraphical restriction. In Lincolnshire they occur mainly within the Dalby, Bigby, Candlesby and Louth Members all in the upper part of the Ferriby Formation. The fluids responsible appear to have entered through the Caistor Fault and the Wash Line, whereas those at Speeton access was through the Flamborough Head Fault Zone.

Direct evidence of the composition of the invasive fluids is lacking but their effects give indication of their nature. Two possibilities are suggested, both are based upon the premise that H_2S or HS^- is responsible for the reduction of the red hematitic pigment or its postulated praecursors – $Fe(OH)_3$ or a range of hydrated ferric oxides. The first, the **external hypothesis**, is that the H_2S or HS^- is generated in a restricted reservoir of sulfate-rich pore fluids by sulfate-reducing bacteria and this entered the Chalk, reduced the ferric iron to ferrous iron, and from these fluids the iron sulfide nodules precipitated. In this situation the increasing $\delta^{34}S$ of the growing nodule reflects the evolving isotopic composition of the sulfate reservoir through the action of bacterial sulfate reduction. The second possibility, the **in situ hypothesis** – originally suggested by Jeans *et al.* (2014) – involves the invasion of the Chalk by a hydrocarbon-rich fluid containing sulfate and sulfate-reducing bacteria from a restricted sulfate reservoir that had already undergone enrichment in $\delta^{34}S$. In this situation the generation of H_2S or HS^- by sulfate-reducing bacteria and the evolution of the $\delta^{34}S$ values towards heavier values evident in the iron sulfide nodules is carried out in place. A variation of this is that the sulfate-reducing bacteria, probably in a dormant phase, were already located in the Chalk . Both hypotheses can explain the change in chemistry evident in the late stage cements associated with sulfidization combined with the loss of overpressure (see above and Text-fig. 20). In the **external hypothesis** the isotopically light carbon from the oxidation of organic matter by the sulfate reducing bacteria ends up as carbonate or bicarbonate in the fluid bearing the H_2S or HS^- into the Chalk. In the **in situ hypothesis** this would have occurred within the Chalk itself.

Hardground development and the loss of red pigment

The diagenesis associated with relatively reduced sedimentation rates and hardground development play a role in the loss of the ferric hydroxide from potentially coloured chalks (Jeans 1980). Hu *et al.* (2012) have discussed this in relationship to the geochemical patterns preserved in the calcite cement associated with terebratulid brachiopods. On a regional scale this loss can best be followed by tracing from Speeton the thicker and coloured chalks of the Belchford and Stenigot Members of the Ferriby Formation into the reduced sequences of the Midland Shelf (Jeans 1980, fig.1). In the Belchford Member the deep red coloured chalks at Speeton (2.37 metres) are replaced by pale pink or ochreous chalks on the Market Weighton Block (~0.04 metres). South of the Market Weighton Block on the Midland Shelf these thicken (~ 0.48 metres) and consist of an upper discoloured zone associated with a glauconitized



Text-fig. 21. The volcanogenic clay mineral –lithofacies association at Folkestone in the Gault Clay, the Melbury Marly Chalk and the Zig Zag Chalk. This is characterized by a smectite-mica clay assemblage, glauconite-rich secondary volcanogenic deposits, and enhanced Fe^{2+} values in the bulk biogenic calcite hardground and a lower zone of pale coloured chalk. The Stenigot Member at Speeton (~2.17 metres) with its pink and purplish wisps is much reduced in thickness on the Midland Shelf (~0.72 metres); it loses its colour completely and is represented by the Lower and Upper *Inoceramus* Beds. These beds consist of coarse-grain chalk made up very largely of the comminuted fragments of Inoceramid bivalves and chalk pebbles. Whole valves of inoceramids may occur and their inner surfaces are typically stained greenish with glauconite (*sensu lato),* patches of rusty staining are sometimes present and these could indicate the former presence of iron sulfides. Some of the chalk pebbles are coated by a very thin skin of glauconite (*sensu lato*), whereas others are stained with glauconite, which penetrates some distance into the pebble. Hu *et al.* (2012) suggest that this loss of hematite pigment on the shelf area reflects the enhanced amount of organic matter introduced into the sediment by its infauna, thus allowing suboxic/anoxic conditions to develop with the microbially mediated reduction of the ferric hydroxide, the precipitation of glauconite and possibily the development of iron sulfides.

Origin of the red pigment

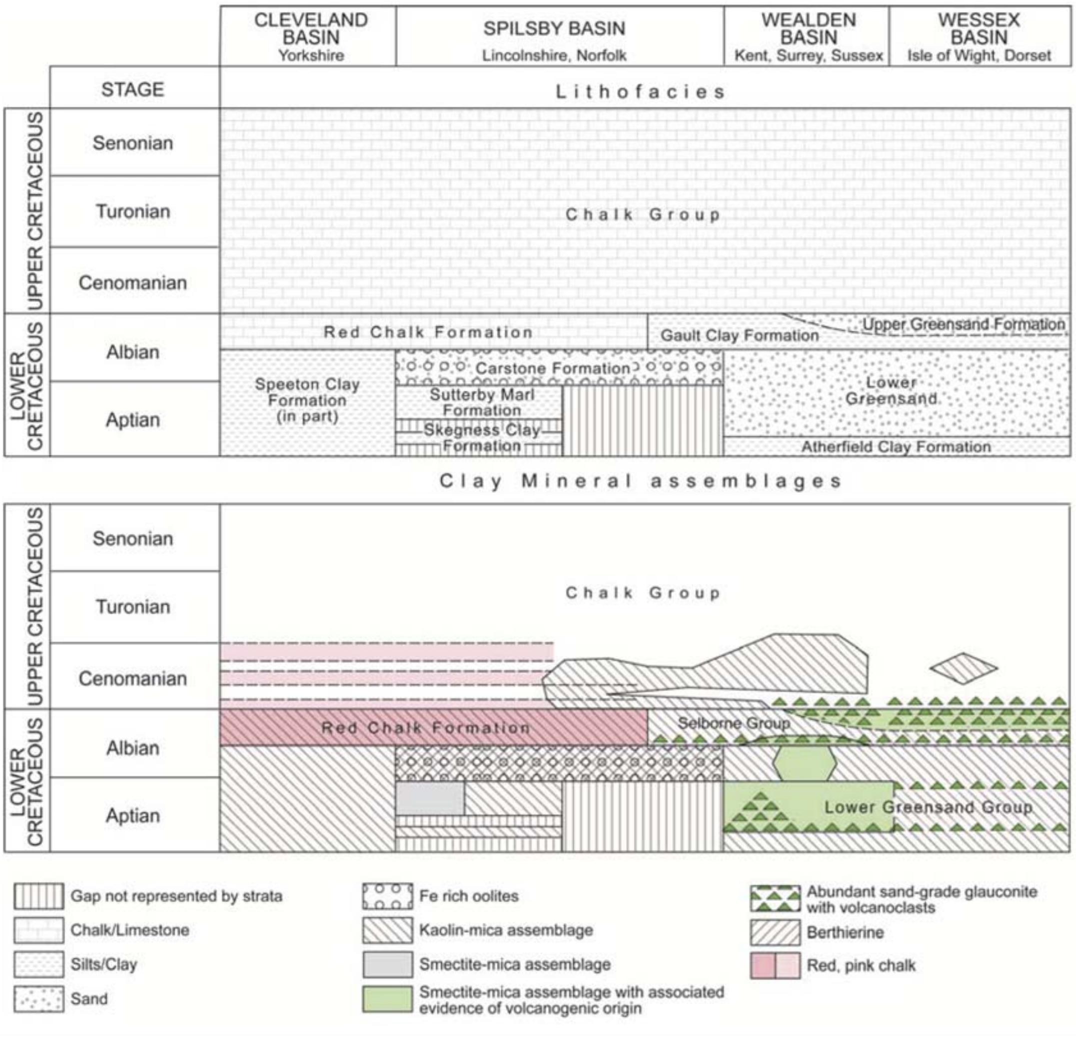
It has already been argued (Jeans 1973) that the source of the hematite responsible for the red colouration of the Mid- and Late- Albian Red Chalk and, by implication in also the immediately overlying Cenomanian Chalk, was derived neither from bauxites nor from Triassic red beds nor from Devonian red beds. The clay mineral assemblages of these suggested sources do not match the clay mineralogies of the red chalks and there is no evidence that a particular clay mineral assemblage is associated with red coloured chalks. Jeans (1973, p. 444) suggested that the hematite was "present, originally in a different form, very soon after deposition because it had been affected by type-1 lithification (hard-ground development)". If the hematite was of detrital origin it is then difficult to explain how it has been dissolved in the well-buffered but anoxic conditions in the chalk sediment associated with the early diagenetic development of hardgrounds. Under such conditions hematite is considered stable in the presence of hydrogen sulfide. If however ferric hydroxide was the original parent of the hematite it would have been readily reduced in the chalk sediment by the hydrogen sulfide from sulfate-reducing bacteria in the anoxic zone of diagenesis.

Two hypotheses have in recent years been put forward for the origin of the hematitic pigment in the Red Chalk Formation —the volcanic or hydrothermal hypothesis of Jeans *et al* (2000) and the microbial hypothesis of Andrews *et al.* (2015).

The **volcanic or hydrothermal hypothesis** is based upon the observed inter-relationship between the regional distribution of clay assemblages, hematitic pigment and the iron contents of the bioclastic calcite in the Red Chalk Formation and its coeval strata in southern England. The Red Chalk Formation (0.5 to 16 metres) represents deposition in Eastern England. Southwards from Hunstanton it passes laterally into the much thicker sequence (up to ~ 155 m; Gallois and Morter 1982, fig.4) of grey marine clays and silty clays of the Gault Clay Formation. The upper stratigraphical part of the Gault passes laterally and westwards into the Upper Greensand Formation— a series of marine sands, glauconitic sands, and clayey sands which may be spiculiferous containing α-quartz and opal-CT silicifications (Jeans 1978). Both the Gault Clay and Upper Greensand contain evidence of the former presence of considerable amounts of volcanic glass/ash that was washed into the Cretaceous Sea by local rivers draining ash covered islands (Jeans *et al.* 2000; Jeans 2006). Once in the marine environment the ash was altered to the smectite-mica clay assemblage. This took place probably during the earliest stages of diagenesis or perhaps even to some extent within the water column as no evidence of glass has been recorded from phosphatic nodules formed during early diagenesis.

The distribution of iron is strikingly different in the Red Chalk, the Gault Clay and the Upper Greensand. In the Red Chalk, iron is largely restricted to the red hematitic pigment where it may reach values of up to 13 wt % of "free iron oxide" in the total rock (Jeans 1973, 1980): glauconite is largely absent; iron sulfides are absent except where they have developed in late diagenetic sulfidization zones: and the iron content of the calcite from the shells that lived in the Red Chalk Sea is low (<5 to 250 ppm). In the Gault Clay red hematite pigment is absent other than at a few levels in East Anglia (Gallois and Morter 1982), while iron sulfides are widespread. Glauconite may be abundant at certain levels. The iron content of the calcite shells of organisms preserved in the Gault is much higher than in the Red Chalk (790 to 4470 ppm). At Folkestone (Text-fig. 21) the iron concentration in the shell calcite shows a pattern related to that of the clay mineral assemblages (Jeans *et al.* 2000, fig. 12). The shell calcite associated with the detrital clay assemblages has an iron (Fe^{2+}) concentration in the range of 790 to 3250 ppm (23 samples averaging 1512 ppm) whereas the iron concentration associated with the volcanogenic smectite-mica assemblage may be even higher with peak values of up to 4470 ppm (11 samples, averaging 3014 ppm). It is postulated that the waters of the Gault Sea were low in oxygen and particularly rich in dissolved iron, either from a hydrothermal source or released from the argillization of iron-rich ash within the water column. This high iron concentration is reflected in the enhanced iron content of the calcitic skeletons of organism living in the Gault Sea. When these iron-rich waters circulated in the shallow, well-oxygenated Red Chalk Sea in eastern England the iron was precipitated out as $Fe(OH)_3$.

The question is to what extent can this hypothesis be applied to the occurrences of hematitic pigment in (1) the Cenomanian and Turonian Chalk of eastern England and further afield in the southern North Sea, Helgoland and northern Germany, and (2) in the higher levels of the Chalk in the North Sea (Text-fig. 1)? Text-fig. 22 displays a schematic plan of the occurrence of the various clay assemblages in England during the interval from Mid Albian to Late Upper Cretaceous times. If the pattern of volcanogenic smectite-mica clay assemblages developed in Albian times is used as a proxy for a volcanic or a hydrothermal iron source it is clear that the same pattern continues throughout the Upper Cretaceous of the British Isles. Other than the appearance of the Chalk lithofacies, the detrital kaolin-mica clay mineral pattern persists independently although perhaps displaying a more distal facies. The smectite-mica clay assemblage has become more extensive, however evidence of its volcanogenic origin has been weakened, possibly because the volcanic sources are more distant. Our working hypothesis is that the stratigraphical intervals where relatively intense red colouration may be preserved under oxic or suboxic conditions represent phases when enhanced amounts of hydrothermally sourced iron were released into the Northern Province. Red coloured chalks of Albian, Cenomanian and Turonian age are present in the southern



Text-fig. 22. Stratigraphical and regional lithofacies and clay mineral variation in the upper part of the Lower Cretaceous and in the Upper Cretaceous strata of the British Isles showing the distribution of the main red and pink coloured chalks (after Jeans 2006, figs 3, 4) part of the North Sea, Helgoland and northern Germany and these, by their geographic association and their stratigraphic age, can be linked to the occurrences in eastern England. There is no lack of evidence – in the form of glauconitised volcanoclasts that may make up to 65% of particular grain size fractions – of submarine volcanism in the glauconitic sands and marls at the base of Chalk sequences in England and Northern Ireland (Jeans *et al*. 1982). These glauconitic beds range in age from Early Cenomanian to Mid Campanian and they hint that spasmodic influxes of iron-rich hydrothermal fluids into the Chalk were frequent as the ocean crust fractured as North America and Europe drifted apart. Text-fig. 1 shows that some of the red horizons in the North Sea coincide with influxes of planktonic foraminiferids from the warmer water of Tethys. These influxes are linked by Haydon Bailey and Liam Galagher (personal communication) to certain sediments of volcanogenic origin.

The **microbial hypothesis** of Andrews *et al*. (2015) is based upon the reinterpretation of the stromatolitic structures recorded by Jeans (1980) from the uppermost part of the Red Chalk Formation at Hunstanton . It is suggested that these are related to *Frutexites*, a problematic microbial structure that has been linked with red limestones in other geological situations. Andrews *et al.* (2015) suggest that these may represent microbes that colonized the suboxic-anoxic boundary in the sediment and these effected the precipitation of ferric hydroxide from anoxic ferrous iron-enriched pore fluids that migrate upwards as the result of compaction from the underlying sediment. Evidence that this hypothesis is responsible for the general red colour of the Red Chalk of eastern England is limited. Such stromatolitic structures have only been recorded in the Red Chalk at Hunstanton and at Goodmanham (Jeans 1980, fig.14). Similar structures are known from the base of the Ferriby Formation in south Lincolnshire at Dalby, Belchford and Stenigot (Jeans 1967). There is no record of their presence in either the Upper and Lower Pink Bands of Bower and Farmery (1912), or the red Cenomanian chalk of Helgoland (Wood and Schmid 1991), or in the red chalks of Late Cenomanian, Early Turonian, and Mid Turonian age in northern Germany (Brochterbeck Formation: Rotpläner: Söhlde Formation). Wiese (2009) has suggested that the red colouration in the Rotpläner (Söhlde Formation) may have been caused by microbial iron fixation during their early diagenesis in spite of the absence of any evidence of stromatolitic structures associated with the red pigment. Present evidence favours the volcanic or hydrothermal hypothesis.

CONCLUDING DISCUSSION

The range of $\delta^{34}S$ displayed by iron sulfide nodules in the Cenomanian Chalk of England has provided a preliminary framework that allows the different patterns of their occurrence to be linked to (1) the relative timing of their development, (2) the presence or absence of coloured chalks, and (3) the geological history of their host chalk. This diagenetic framework can be improved further in two ways. First, the earliest stages in the development of iron sulfides needs more attention in particular to (a) the fine-grained sulfides associated with the mouldic cavities left after the aragonite of various invertebrate shells in the Chalk sediment had been dissolved after burial, and (b) the early iron sulfides associated with hardground development of which there are usually only rusty traces. Second, the highly oxidised state of many former iron sulfide nodules means that suitable material is not available for analysis: in this study this applies particularly to inland exposures of the Ferriby Chalk (as well as the younger overlying chalks) in eastern England where coherent nodules may have been relatively common but only occasionally is there any unoxidised material preserved, let alone enough to determine the range of values that represent the growth of the nodule. There is, in addition, the sampling problem with the incoherent nodules, such as at Speeton where the full range of $\delta^{34}S$ values may not have been realised in this study. More detailed sampling could overcome this.

The antipathetic relationship between the occurrence of coloured chalk and the development of iron sulfide nodules is a complicated one. It can develop at various and at different scales during intrinsic and non-intrinsic diagenesis. On a regional scale there is an intrinsic difference during the deposition of the Mid Albian to Late Cenomanian sediments of England. In southern England relatively rapid sedimentation and burial of organic matter has meant that all the sediments underwent anoxic diagenesis with the loss of any ferric hydroxide present. Only occasionally in East Anglia (Gallois and Morter 1982 record instances in the Gault) is there hematite pigment suggesting that locally there was insufficient organic matter in the sediments to carry them over into the anoxic zone of diagenesis. This general lack of evidence of the oxic and suboxic zones of diagenesis does not mean that the sediments did not pass through these zones. In eastern England, in contrast, sediment accumulation was slower and it is possible that all the organic matter was oxidised before anoxic diagenesis could develop. This resulted in coloured bands being preserved at levels where the concentration of ferric hydroxide was relatively high. During the oxic and suboxic phases of diagenesis there is evidence that some ferric hydroxide was lost as it was metabolised and incorporated into very early calcite cements without the precipitation of iron sulfides. It was only when additional organic matter was introduced by active in-faunas associated with hardground development and very early lithification (Types 2 and 3, Jeans 1980) in eastern England that anoxic conditions develop with the complete dissolution of the ferric hydroxide.

Conspicuously disrupting this pattern in eastern England is the unrelated invasion by sulfate and hydrocarbon rich solutions entering the Chalk initially through faults, but then penetrating huge volumes of the over-pressured Cenomanian reservoir as it collapsed. This resulted in anoxic conditions as the result of bacterial reduction and the consequential dissolution of the ferric hydroxide pigment with the precipitation of iron sulfides. If the waxing and waning of the input of iron from hydrothermal or volcanic sources into the Albian, and Late Cretaceous seas is the origin of the hematite pigment such levels of coloured chalks could be of stratigraphic use as long as it is realised that they may be lost either during intrinsic or non-intrinsic diagenesis. This suggests that their use for correlation may be limited.

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