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Regional hardening of Upper Cretaceous Chalk in eastern England, UK: trace element and stable isotope patterns in the Upper Cenomanian and Turonian Chalk and their significance

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ABSTRACT:

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The regional hardening of the Late Cenomanian to Early Turonian Chalk of the Northern Province of eastern England has been investigated by examining the pattern of trace elements and stable carbon and oxygen isotopes in the bulk calcite of two extensive and stratigraphically adjacent units each 4 to 5 m thick of hard chalk in Lincolnshire and Yorkshire. These units are separated by a sequence, 0.3–1.3 m thick, of variegated marls and clayey marls. Modelling of the geochemistry of the hard chalk by comparison with the **Standard Louth Chalk,** combined with associated petrographic and geological evidence, indicates that (1) the hardening is due to the precipitation of a calcite cement, and (2) the regional and stratigraphical patterns of geochemical variation in the cement are largely independent of each other and have been maintained by the impermeable nature of the thin sequence of the clay-rich marls that separate them. Two phases of calcite cementation are recognised. The first phase was microbially influenced and did not lithify the chalk. It took place predominantly in oxic and suboxic conditions under considerable overpressure in which the Chalk pore fluids circulated within the units, driven by variations in compaction, temperature, pore fluid pressure and local tectonics. There is evidence in central and southern Lincolnshire of the loss of Sr and Mg-enriched pore fluids to the south during an early part of this phase. The second phase of calcite precipitation was associated with the loss of overpressure in probably Late Cretaceous and in Cenozoic times as the result of fault movement in the basement penetrating the overlying Chalk and damaging the seal between the two chalk units. This greatly enhanced grain pressures, resulting in grain welding and pressure dissolution, causing lithification with the development of stylolites, marl seams, and brittle fractures. Associated with this loss of overpressure was the penetration of the chalk units by allochthonous fluids, rich in sulphate and hydrocarbons, derived probably from the North Sea Basin. Microbial sulphate-reduction under anoxic conditions within these allochthonous fluids has been responsible for dissolving the fine-grained iron and manganese oxides within the chalk, locally enriching the Fe and Mn content of the calcite cement. The possibility is discussed that the pattern of cementation preserved in these regionally hard chalks of Late Cenomanian and Early Turonian age may be different from that preserved in the younger (late Turonian to Campanian) more basinal chalks of eastern England.

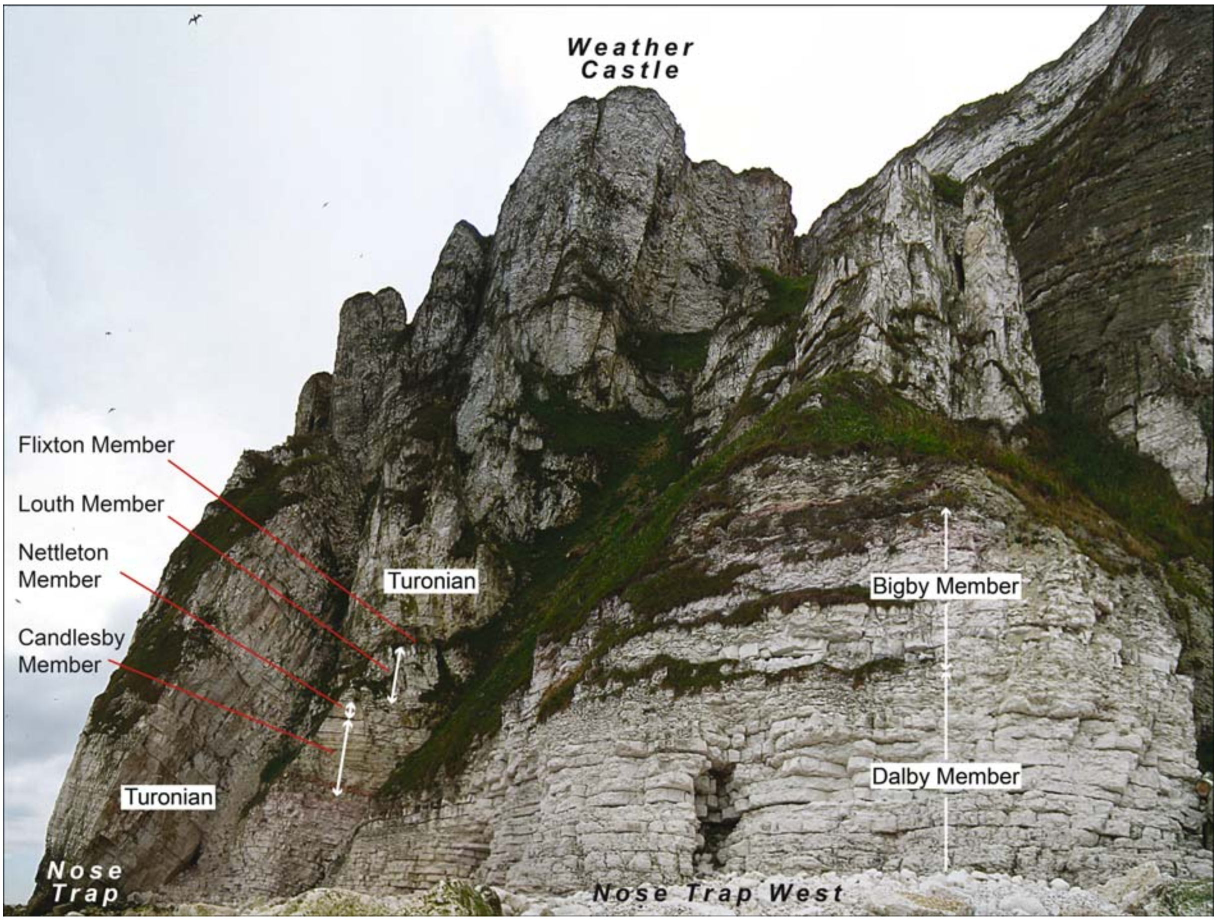
Key words: Chalk hardening; Trace elements; Stable isotopes; Cement modelling; Reservoir diagenesis; History.

INTRODUCTION

The Upper Cretaceous Chalk varies regionally and stratigraphically from a soft friable sediment to a hard fine-grained chalky limestone. Jukes-Browne and Hill (1903, 1904) in their synthesis of the Upper Cretaceous rocks of Britain were perhaps the first to differentiate between early diagenetic cementation responsible for hardgrounds and nodular chalks and the cementation responsible for the regional differences in hardness. Hill (in Jukes-Browne and Hill 1903, 1904) provided data showing the weight percent acid insoluble residues from biostratigraphical equivalent zones in southern and eastern England that effectively compares soft with regionally hardened chalks. These values show no systematic difference suggesting that the hardening was no more than the internal rearrangement of the calcite and the acid insoluble residue.

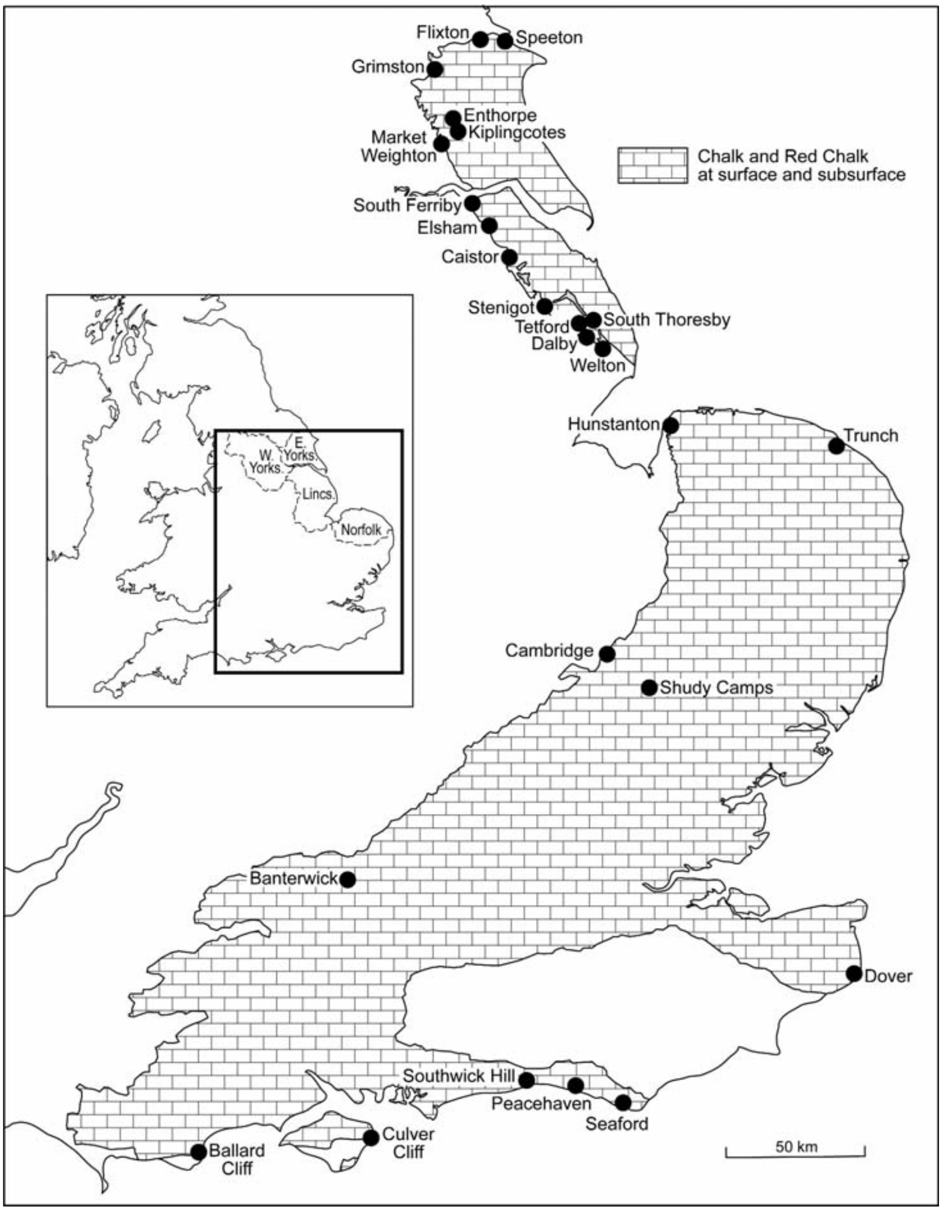
Differences in the regional hardness of the Chalk in the British Isles have been commented upon for well over a century and in more recent years have been the topic of scientific investigation (Hu *et al.* 2012 for review). Particular attention has been paid to the Chalk of Northern Ireland (Wolfe 1968; Scholle 1968; Maliva and Dickson 1997), the Chalk affected by post-Cretaceous east-west folding in England (Mimram 1975, 1977, 1978), and the Chalk hydrocarbon reservoirs of the North Sea Basin (e.g. Scholle 1968; Oakman and Partington 1998). The understanding of the mechanism and conditions under which the regional hardening took place is an important aspect of predicting its properties, particularly when the Chalk is involved with major engineering projects or for the extraction of water, oil and gas trapped within reservoirs.

Recent progress in understanding the early lithification and cementation of the Chalk in eastern and southern England (Hu *et al.* 2012; Jeans *et al.* 2012) has provided a firmer basis from which the regional hardening can be considered. This investigation is an attempt to resolve the origin of the hard chalk of eastern England (Text-fig. 1) that lacks evidence of early lithification. It first appears as the predominant lithology in the upper-



Text-fig. 1. Hard Northern Province Chalk in the Buckton Cliffs at Nose Trap, near Speeton, Yorkshire, UK, This exposes various members (Dalby, Bigby, Candlesby, Nettleton, Louth) from the middle and upper part of the Cenomanian Ferriby Formation and the Flixton Member of the overlying, Welton Formation (predominantly of Turonian age). Details of the stratigraphy and location are given, respectively, in Text-fig. 4 and in Hu *et al.* (2012, Text-fig. 5) most part of the Cenomanian Ferriby Formation and continues through the overlying White Chalk of Turonian to Campanian age. The distribution of this hardened chalk coincides generally with that of the Northern Chalk Province in eastern England which is also associated with, or characterized by, various intrinsic features including particular fossil assemblages, pink and red chalks, and tabular and carious flints.

Previous investigations have presented rather contradictory evidence for the origin of the hardening. Mimram (1978) suggested that the hardening was due to the precipitation of a cement from porewaters of meteoric origin introduced at a relatively early stage of diagenesis prior to the Chalk being affected by tectonism; Scholle (1974) suggested a cement resulting from the precipitation from a mixture of the original chalk pore water with meteoric water combined with the effects of enhanced geothermal gradients. The objective of our investigation has been to clarify the nature of the hardening of the Chalk and its relationship to the intrinsic diagenesis of the Chalk of the Northern Province. The approach we have taken is novel — although Jeans (1980, pp. 89–99) used similar methods in a preliminary investigation — and is based on modelling using the soft, unhardened chalk in south-east England as a starting point. This side-steps the intrin-



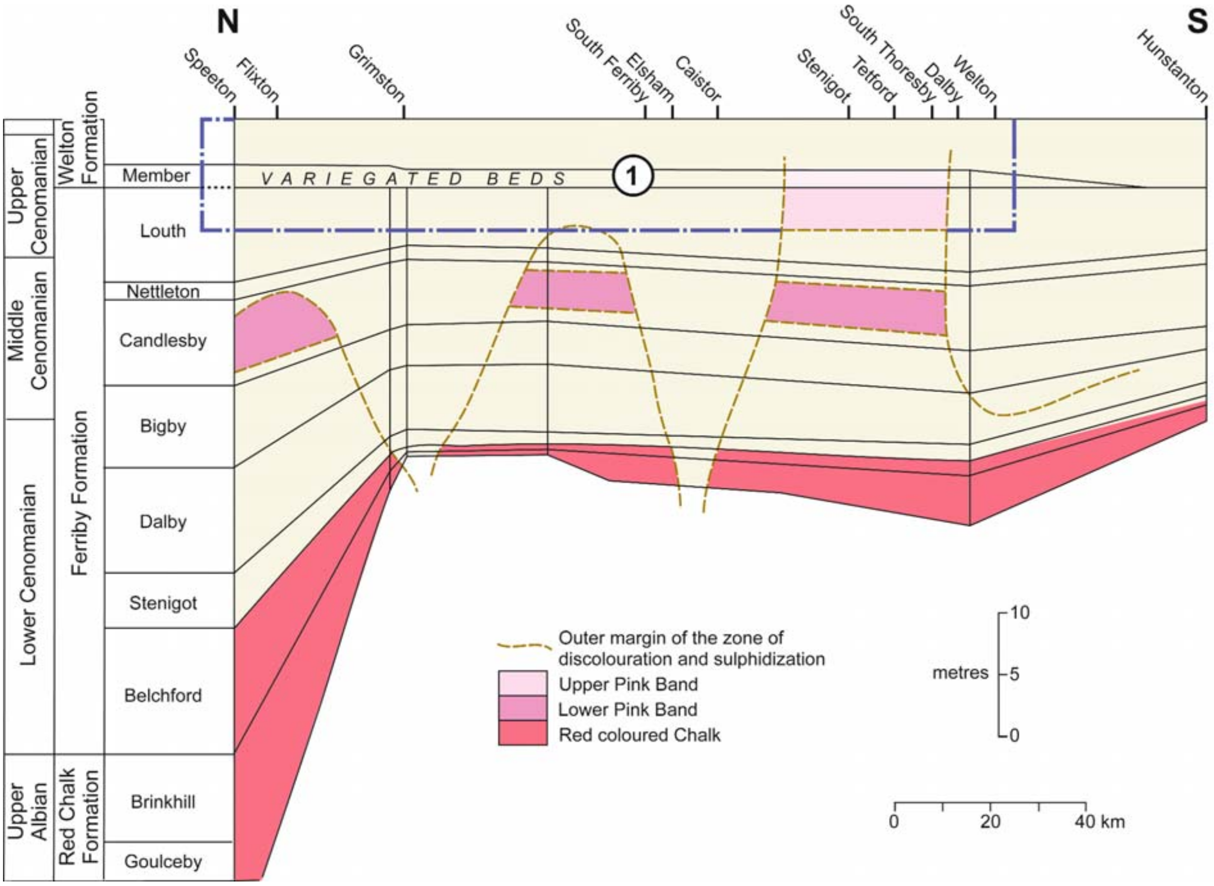
Text-fig. 2. Distribution of the Upper Cretaceous Chalk at the surface and subsurface in the UK showing the locations mentioned in the text and in Hu *et al.* (2014). The insert shows the county names (East Yorkshire: Lincolnshire: Norfolk) referred to in the text sic problems resulting from the extremely fine-grain of the Chalk, the nature of its alteration during diagenesis, and the limitation of electron microscopy, however, our approach may introduce its own problems and these are fully discussed.

This paper is based on the detailed analysis of two units of hard chalk of Late Cenomanian and Turonian age that occur throughout Lincolnshire and Yorkshire. Lithostratigraphically they represent the first major occurrence of regionally hardened chalk in eastern England. For each of these units of hard chalk we describe (1) the general lithology, (2) the bulk specific gravity, and (3) the regional trace element (Fe, Mn, Mg, Sr) and stable isotope ($\delta^{13}C$, $\delta^{18}O$) geochemistry of the bulk calcite. Comparison with the unhardened chalk at Dover in south-east England has allowed us to deduce that the hardening is related to calcite cementation and to model the regional patterns of variation in trace elements and stable isotopes of the cement. Comparison of these model patterns with regional geological features – patterns of faulting, zones of sulphidization, subsurface distribution of igneous bodies in eastern England and the nearshore parts of the North Sea – provides additional evidence of the factors controlling the Chalk hardening.

Locations mentioned are shown in Text-fig. 2.

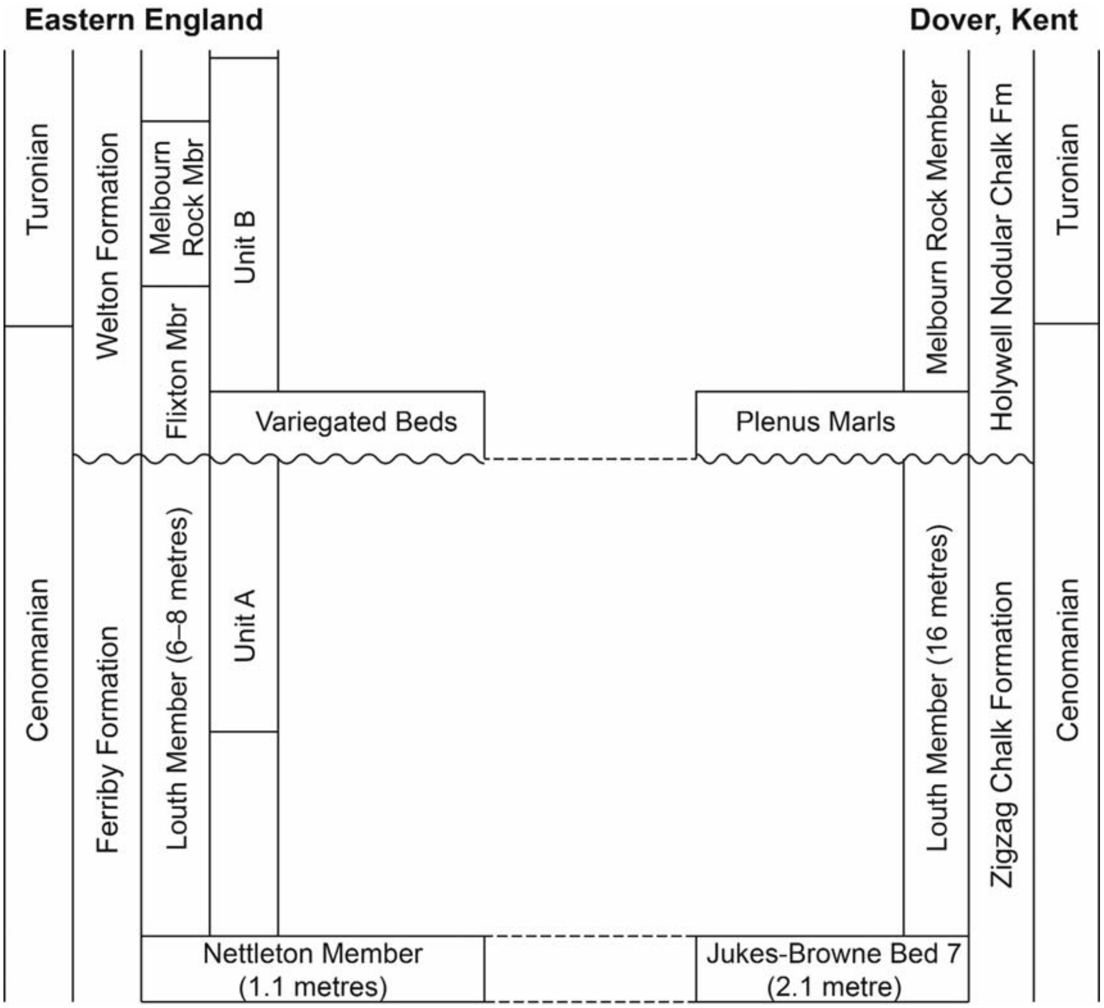
SAMPLE STRATIGRAPHY

The stratigraphical terms used are shown in Text-figs 3 and 4. Text-fig. 3 shows the horizontal section of the chalk that has been investigated in the Ferriby and Welton formations in eastern England and its relationship to the zones of sulphidization that cross-cut these formations. A number of these lithostratigraphic terms need further explanation. In eastern England, the term Variegated Beds (Wood and Mortimore 1995; Wood *et al*. 1997) is preferred to the Plenus Marls/Black Band. This thin unit of marls and marly clays rests on the sub-Plenus erosion surface but it is only in part the regional development of the Plenus Marls Member of the Holywell Nodular Chalk Formation of southern England (see discussion in Mortimore *et al*. 2001). More-



Text-fig. 3. 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. Zone 1 indicates the stratigraphical and regional extent of the detailed investigation of chalk hardening over, as their name implies, the Variegated Beds display lateral and vertical variations in colour between red, grey, green, white and black and include one or more well defined black bands (Jeans *et al.* 1991, fig. 10; Wood *et al.* 1997) that are absent from the Plenus Marls. The Louth Member (6–8 m thick in eastern England, 16 m thick at Dover) is a laterally continuous unit of white fine-grained chalk which can be traced from Speeton on the Yorkshire coast and throughout much of southern England. It lies between the base of the Variegated Beds/Plenus Marls and the underlying Nettleton Chalk Member (Jeans 1980) of eastern England and its lateral continuation in southern England, Jukes-Browne Bed 7. It is of late Middle to Late Cenomanian age. The Louth Member of eastern England (6–8 m thick) consists of hardened chalk whereas at Dover it is represented by 16 m of soft chalk. The present stratigraphical scheme used by the British Geological Survey (reviewed in Mortimore *et al.* 2001) does not recognise this unit either in southern England, where it occurs at the top of the Zigzag Formation (Middle to Upper Cenomanian) (Text-fig. 4), or in eastern England where it is within the Ferriby Formation (Lower to Upper Cenomanian). This unit has been recognised in Jeans (1968, fig. 4) and has been referred to as the Louth Member in eastern England (Jeans 1980, fig. 3) and at Dover (Jeans *et al.* 1991, fig. 2).

The Red Chalk Formation (Text-fig. 3) is used in preference to the Hunstanton Limestone Formation. This formation is included within, but must be differentiated from the lowest zone of red coloured chalk shown in Text-fig. 3. This lowest zone consists of red, pink and ochreous coloured chalk. Included in this is the basal dark red stromatolitic part of the Cenomanian section at Hunstanton (Jeans 1980, fig. 12), as well as the thin zone of very pale pink and ochreous chalk in the lower half of the Paradoxica Bed (Jeans *et al*. 2012, text-figs 2, 7; Jeans *et al*. 2014, fig. 8).



Text-fig. 4. Lithostratigraphical and stratigraphical terms used in eastern England and at Dover

The section investigated (Text-figs 3, 5) extends from some 3 to 4 m below the top of the Ferriby Formation up to some 5 m above the base of the overlying Welton Formation. It is divided into two by the laterally continuous marly Variegated Beds. The lower unit, **Unit A,** consists of normal hard chalk that shows no obvious field evidence of early lithification as defined by Jeans (1980). Its base marks the appearance of hard chalk as a continuous facies whereas in the underlying part of the Ferriby Formation occasional beds of this chalk type may occur but are interbedded with chalk and marl showing evidence of early lithification. In south Lincolnshire (Tetford, South Thoresby), where the Upper Pink Band is preserved (Text-fig. 3), the base of Unit A is at or just below the base of this coloured band. The top of Unit A is the sub-Plenus erosion surface, which defines both the base of the Variegated Beds and the Welton Formation. The upper unit, **Unit B,** includes the upper part of the Flixton Member of Jeans (1980), the Melbourn Rock Member of Jeans *et al*. (1991, fig. 12) and some of the overlying chalk (Text-fig. 4). The base of this unit occurs within the upper part of the marly Variegated Beds and is placed at the level at which the calcium carbonate content reaches 80% and over. The upper limit is the band of occasional flint nodules just below the First Main Flint Horizon of Wood and Smith (1978, fig. 2). Unit B contains a number of thin primary marls, 1 to 4 cm thick (Text-fig. 5). The most important of these is the Green Trace Bed with green glauconitic traces, which is recognisable throughout eastern England. Three thin marl seams overlie this and extend throughout Lincolnshire and southern Yorkshire.

Samples were collected from the following eight localities in eastern England that expose all or part of this stratigraphical section: Unit A exposed at Prentice Cove, Buckton Cliffs, Speeton (Jeans 1973, p. 425: grid ref. TA 18307480); Unit B exposed in a small chalk pit at Flixton (grid ref. TA 03937918); Units A and B exposed in chalk pits at South Ferriby (grid ref. TA 03937918), Elsham (grid ref. TA 03851310), Caistor (grid ref. TA 12340025), Tetford (grid ref. TF 32957595), South Thoresby (grid ref. TF 40507725) and Welton (grid ref. TF 45056920). Comparative samples were collected from the Louth Member at the top of the Zigzag Chalk Formation at Dover (Jeans *et al*. 1991, fig. 2 for sample horizons) where the chalk is soft, of low bulk specific gravity and has been essentially unaffected by regional hardening; these samples have been used to establish the **Standard Louth Chalk** which has been used for modelling the extent and chemistry of the cement affecting the Chalk (Jeans *et al.* 2012, 2014).

SAMPLE LITHOLOGY

The regional and stratigraphical distribution of samples in Units A and B is shown in Text-fig. 5. The Louth Member – the upper part forms Unit A – and its uncemented correlative at Dover (Text-figs 4, 6) consist of fine-grained chalk made up predominantly of coccolith debris with varying amounts of calcispheres and planktonic foraminifera. No systematic vertical or lateral variation in lithofacies has been noted in eastern England. Petrological investigation of Unit A has been restricted to the section at Speeton (Text-fig.7). More general views of the Louth Member in the Buckton Cliffs, Speeton, are given in Mortimore *et al*. (2001, fig. 5.24, p. 415) where it is located between the Nettleton Chalk Member and the Variegated Beds. Typical lithofacies are shown in Text-fig. 8. Unit B, in contrast, displays a considerable vertical variation in lithofacies. This has been examined petrologically at Tetford, Elsham and Flixton. Typical lithologies are shown in Text-fig. 9; three lithofacies zones are recognised. The lowest extends from the top of the Variegated Beds up to the base of the “chalk rich in inoceramid fragments”; this consists of a fine-grained coccolith-rich matrix with occasional planktonic foraminifera, calcisphere and inoceramid bivalve prisms (Text-fig. 9A). The middle zone has little fine-grained matrix. It is made up predominantly of broken fragments and single prisms of inoceramid bivalves and calcispheres, fragments of other shelly fossils and occasional foraminifera (Text-fig. 9 C, D). The lower part of this zone is characterised by large inoceramid bivalve shell fragments that are conspicuous in the field and is the band of “chalk rich in inoceramid fragments” shown in Text-fig. 5. The upper part becomes increasingly enriched in calcispheres (Text-fig. 9B) and at about a metre from the top of Unit B it grades into the upper zone. This consists of a fine-grained coccolith-rich chalk with fairly abundant calcispheres and planktonic foraminifera (Text-fig. 9A). Lateral changes in lithology are evident between Flixton in the north and the more southerly locations. At Flixton the chalk is thinly bedded, occurring typically in beds 10 to 15 cm thick each separated by a thin seam of marl (Jeans *et al*. 1991, fig. 10), compared to the more massive chalk to the south which occurs in beds typically 25 cm or more in thickness.

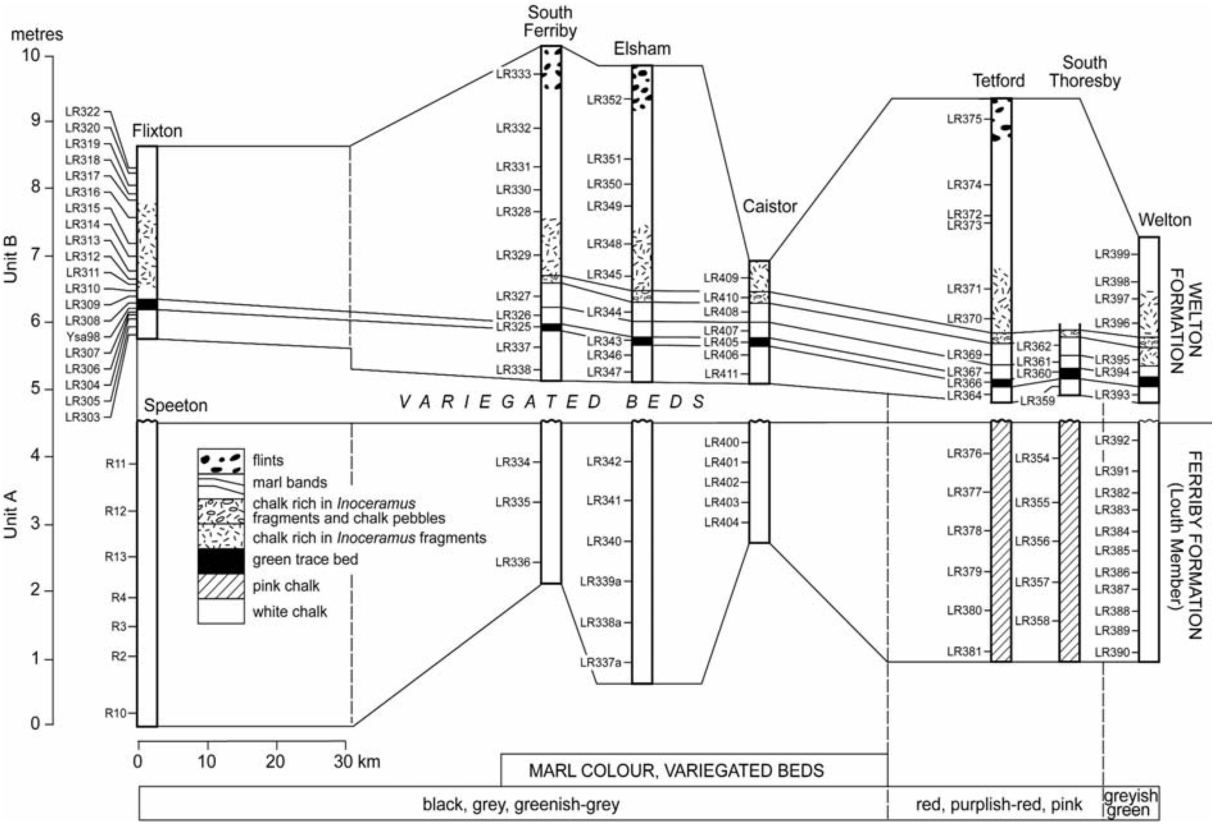
ANALYTICAL METHODS

The geochemistry, bulk specific gravity (SG) and acid insoluble residues (AIR) of chalk samples were determined by the following methods. Bulk specific gravity measurements used the procedure described by

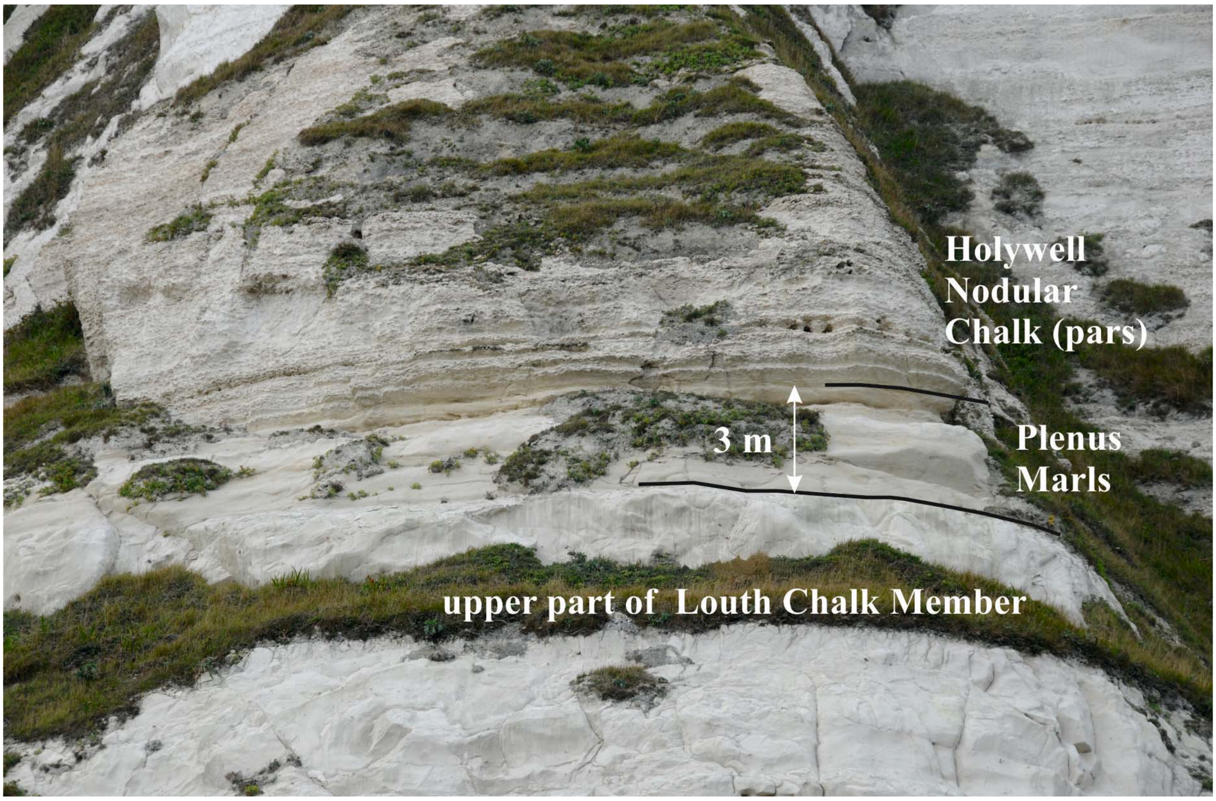
Jeans (1980, p. 155; this is similar to BS 1377, 1975) using wax coated blocks of chalk (dried at 105°C) weighed in air and then in water. Samples for chemical analysis were initially crushed, split and then ground finely by hand. The percentage weight of acid insoluble residue was determined by dissolving 1g of oven-dried material (105ºC) in exactly 25 ml standard volumetric 1 molar HCl. The excess acid was titrated against standard volumetric 1 molar NaOH using Bromocreosol Green as indicator. From this the weight percent $CaCO_3$ was calculated and the AIR was obtained by difference. Prior to titration it is essential that the AIR be removed by filtration through Whatman No. 42 filter paper. Chemical analysis was restricted to chalks with a content of $CaCO_3$ of 80 wt % and over. A total of 120 samples were analysed. The concentrations of trace elements (Fe, Mn, Mg, Sr) in the bulk calcite were determined with a Perkin-Elmer Absorption Spectrophotometer (model 2280) or by colorimetry (Jeans 1980, p. 156 for Fe). Correction was made for the content of acid insoluble residue. Samples were prepared by dissolving 0.25 gm of oven dried sample in excess cold 1 molar acetic acid, filtered through Whatman No. 42 filter paper, and made up to precisely 50 ml with distilled water.

Stable isotope analysis was performed at the Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge. Samples were analysed for $^{18}O/^{16}O$ and $^{13}C/^{12}C$ 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 δ‰ values with reference to the VPDB and the precision was better than +/–0.06 per mil for $\delta^{13}C$ and +/–0.06 per mil for $\delta^{18}O$.

Contouring in Text-figs 11–16 was carried out manually based on the actual and model chemical data (Tables 3, 4) for Units A and B using the precise positions in the horizontal section of the Chalk from which the samples came (Text-fig. 5). The orientation of the contour and the intervals between them were chosen to express best the vertical and lateral variations in values without regard to preconceived assumptions such as, for example, they might be expected to parallel the general direction of bedding or to reflect the arrangement of chalk lithofacies. The robustness of the



Text-fig. 5. Horizontal section through the upper part of the Ferriby Formation and the lower part of the Welton Formation in eastern England showing the position of samples in units A and B that were chemically analysed. Further details of the samples from the Louth Member at Speeton and their stratigraphic relations to other samples that have been investigated in this study as well as by Jeans *et al.* (2012) and Hu *et al.* (2014) are shown in Text-fig. 7



Text-fig. 6. The cliff section at Samphire Hoe, Dover, UK, showing the chalk of the upper part of the Louth Member (Zig Zag Chalk Formation), the Plenus Marls, and part of the overlying Holywell Nodular Chalk Formation

regional patterns of contours is variable. It is strongest in the southern and central regions where the distance between sampling locations averages about 10 km. It is the weakest in the 30 km and 60 km gaps between, respectively, southern Lincolnshire and central and northern Lincolnshire and northern Lincolnshire and East Yorkshire (Flixton/Speeton). Sample intervals (Text-fig. 5) were chosen to investigate general trends as well as lithological variations; they varied from about a metre at the maximum to less than 10 cm.

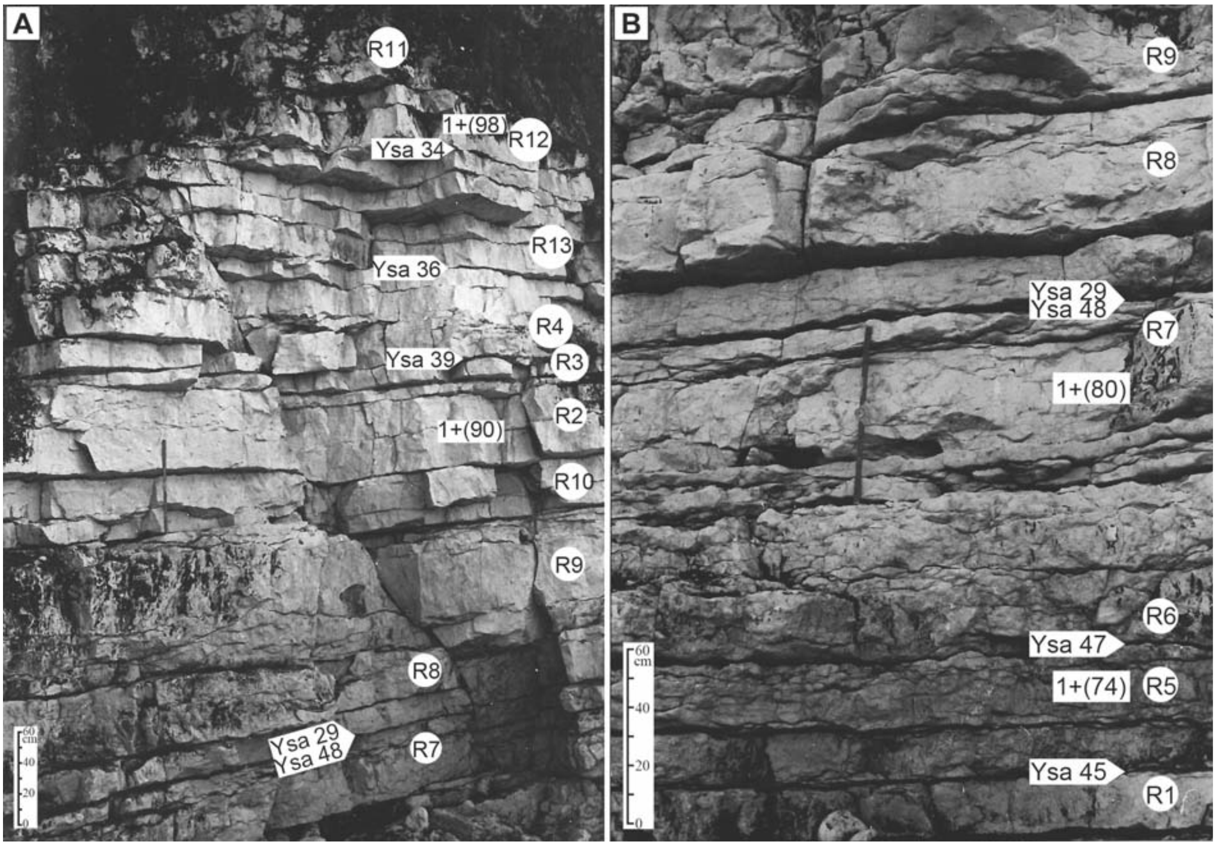
CEMENT MODELLING

The basis of our modelling is that the upper part of the Louth Member at Dover is (1) of the same stratigraphic age (*Calycoceras guerangeri* ammonite Zone), (2) essentially unhardened and has been little affected by calcite cementation or pressure dissolution, and (3) it represents the upper part of the Louth Member in eastern England in its primary lithofacies, chemical composition and degree of compaction prior to its hardening. There are some conspicuous differences between eastern England and southern England but these are of post-depositional origin and not of primary lithofacies. In eastern England there are thin marl seams of post-depositional origin that may be parallel to the general direction of bedding or at a considerable angle to it. For example, in the sea cliffs at Speeton such secondary marl seams are well developed and in any one location divide the sequence into a number of beds (Text-fig. 7). Laterally individual marl seams can be traced for only tens or a few hundreds of metres before they die out and thus the pattern of beds is always changing along the cliff section. Their lithological investigation (Jeans 1980, pp. 89–96) and their patterns of stable isotopes (Jeans *et al.* 2012, table 4; Hu *et al.* 2014, table 4) indicate that they were formed by pressure dissolution during late diagenesis. There are some conspicuous differences between eastern and southern England in the presence or absence of diagenetic iron sulphides or red hematitic pigments. The Louth Member in eastern England may contain red and pink units of chalk (Text-fig. 3) where they have not been affected by late-stage diagenetic sulphidization, whereas in southern England there is no evidence of this colouration but pyrite is widespread. These differences have little effect on the modelling as we are only concerned with the geochemistry of the calcite fraction and these processes have played at the most a minor role in affecting the geochemistry of the bulk calcite.

The following questions are important in the investigation of the process of hardening and the associated increase in bulk specific gravity of the chalk. Has it been caused by pressure dissolution in (1) an essentially closed system where the dissolved bioclastic calcite is reprecipitated in the adjacent pore space, or (2) by pressure dissolution in an open system where the dissolved $CaCO_3$ is lost in the escaping pore waters and the hardening is the result of a more intimate interlocking of the grains and possibly grain crushing? Or has it been caused by the precipitation of calcite cements perhaps similar to those associated with early lithification (Hu *et al.* 2012)?

Two terms used in the modelling need clarification. **Pore-space loss (PSL)** refers to the loss of pore space that is calculated from the difference in bulk specific gravity (SG) between the **Standard Louth Chalk** and the actual sample of hard chalk. **Model cement** is the term used when the **pore-space loss** is the result of the precipitation of a calcite cement. The percentage by volume of any **pore-space loss** or **model cement** and its geochemistry (referred to as **cement modelling** in this paper) in the hard chalk of **Units A** and **B** has been calculated by assuming that prior to hardening the chalk had similar values of bulk specific gravity, $CaCO_3$ content, trace elements and stable isotopes to the **Standard Louth Chalk,** which is based on the average of eight samples (Table 1) from the Louth Member at Dover. An example of this modelling is shown in Text-fig. 10.

The range of primary chalk lithofacies in the hard chalks of Unit B is much greater than in Unit A. There are no stratigraphical equivalents of similar but uncemented lithologies to act as models for comparison. At Dover, the equivalent strata form part of the Holywell Nodular Chalk Formation (Text-fig. 4), which displays abundant evidence of early lithification. The cement



Text-fig. 7. The Louth Member of the Ferriby Formation exposed at Prentice Cove, Buckton Cliffs, Speeton, Yorkshire. This shows the position of samples investigated in this study, in Jeans *et al.* (2012, table 6) and in Hu *et al.* (2014, table 4). Text-fig. 7A shows the upper part of the Louth Member where Unit A extends down to just below sample R10 and is characterised by a laterally variable sequence of alternating beds of hard homogeneous chalk and marl seams of secondary origin. This passes gradually downwards into interbedded homogeneous and nodular chalks with intervening marl seams which are seen in Text-fig. 7B. The bed numbers (1+(98) etc.) refer to the locations of the thin sections illustrated in Text-fig. 8

modelling in Unit B is less satisfactory as we had to base it upon the **Standard Louth Chalk.** This has sometimes led to a model cement with a negative value of a particular trace element, particularly with Sr, to some extent with Mg, and very occasionally with Fe and Mn. Such values are clearly not realistic for actual cement. Understanding the reasons for these negative values is best done by considering the example of the Sr contents in 5 samples from Unit B. Table 2 shows the pertinent details of these samples. They are assumed to have started off their history as **Standard Louth Chalk** with no cement, a bulk specific gravity of 1.64, and a concentration of Sr (calcite) of 550 ppm. They are arranged in order of the calculated model Sr contents of their cement with values ranging from 31 ppm to -186 ppm. Their bulk specific gravities vary from 1.98 to 2.44 and the **pore-space loss** (assumed cement volume) from 12.5 to 29.5 vol. %. The Sr content of the bulk calcite of the actual samples varies from 329 to 400 ppm, in all cases less than the 550 ppm value of the **Standard Louth Chalk**. In order to modify the chemistry of a sample made from **Standard Louth Chalk** and the additional calcite cement – that is the present hard chalk – to its actual measured value, it is necessary to reduce the Sr concentration in the cement so that their joint average value is the actual value. For four samples in Table 2 even a model calcite cement with no Sr is insufficient to do this; in these circumstances, in order to achieve the actual value, it is necessary to reduce further the average value by subtracting Sr from the system thus giving the model cement a negative value to bring the modelling back into line with the actual values. The actual negative value will depend upon both the amount of calcite cement and the actual Sr value of the hard chalk sample under consideration. The significance of negative model values are three fold: either (1) the **Standard Louth Chalk** is not similar in its chemistry and porosity to the chalk that gave rise to the negative values, or (2) there has been a selected loss of Sr from one or more of the components of the sediment and its removal from the sediment system during diagenesis, or (3) a combination of (1) and (2). Consideration of these patterns of negative values has provided an additional and important insight into the factors that may control the hardening of the Chalk and affect the chemistry of any cement involved.

RESULTS

The bulk specific gravities, trace element and stable isotope composition in the bulk calcite of the chalk samples and their model cement is shown in Tables 3 and 4.

Sample No.	**$CaCO_3$ wt%**	**SG**	**Fe (calcite) ppm**	**Mn (calcite)ppm**	**Mg (calcite) ppm**	**Sr (calcite) ppm**	**$\delta^{18}O_{V\text{-}PDB}$ ‰**	**$\delta^{13}C_{V\text{-}PDB}$ ‰**
KR130	95.7	1.54	235	326	1045	531	-2.83	2.77
KR131	95.7	na	235	256	1169	530	-2.76	2.63
KR126	92.9	na	274	329	1169	545	-2.48	2.70
KR132	93.2	1.57	267	325	1170	592	-2.75	2.67
KR133	91.9	na	280	333	1370	602	-3.34	2.56
KR134	93.8	1.59	260	309	1654	574	-3.09	2.66
KR118	94.0	1.75	261	420	1453	466	-3.13	2.41
KR117	88.8	1.75	237	353	1466	547	-2.31	2.57
range	89-96	1.54-1.75	235-280	256-420	1045-1654	530-602	-2.31 to -3.34	2.41-2.77
average	93	1.64	256	331	1312	548	-2.84	2.62

na - data not available

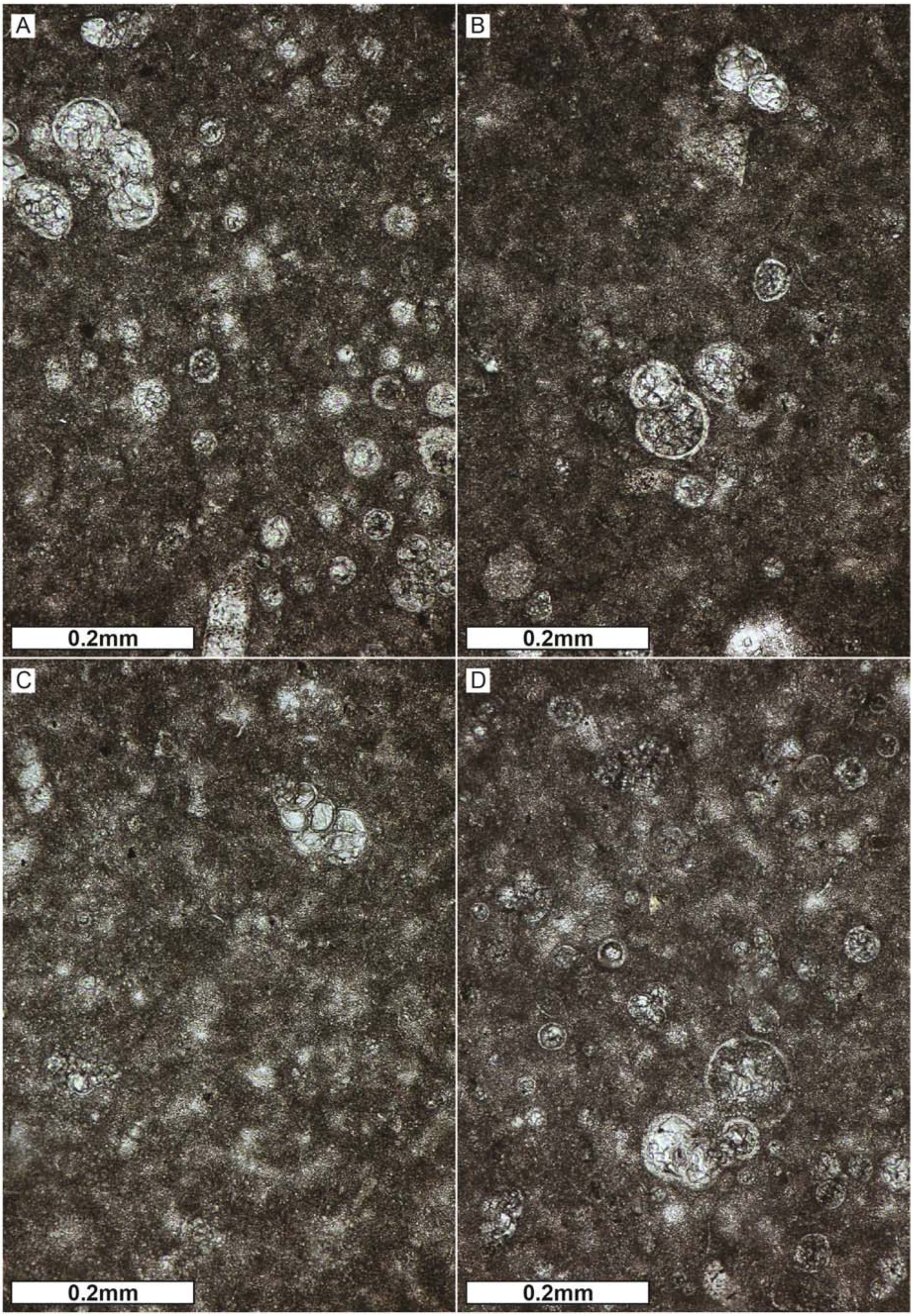
Table 1. $CaCO_3$ contents, bulk specific gravity, acid insoluble residues, trace element concentration and stable isotope values in the bulk calcite of 8 samples from the Louth Member (*sensu* Jeans *et al.* 2012) at Dover, Kent, used to establish the **Standard Louth Chalk** for modelling

sample	location	bulk specific gravity (SG)	actual Sr conc.	P-SL/cement vol.%	model cement Sr ppm
LR345	Elsham	2.32	380	25.1	31
LR140	Caistor	2.44	366	29.5	-2
LR360	S.Thoresby	2.16	392	19.2	-42
LR350	Elsham	2.27	329	23.2	-157
LR343	Elsham	1.98	400	12.5	-186

P-SL: Pore-Space Loss

Table 2. Bulk specific gravity, Sr (calcite) of the bulk chalk, volume of pore space loss or cement, model Sr (calcite) of the cement in 5 samples from Unit B, Welton Formation, eastern England

Text-fig. 8. Micrographs of thin sections illustrating the lithofacies of the Louth Member at Speeton , Yorkshire. (A) – Planktonic foraminifera and calcispheres in a fine-grained chalk matrix, Bed 1+(98), Unit A. (B) – Fine-grained chalk with occasional planktonic foraminifera and rare calcispheres, Bed 1+(90), Unit A. (C) – Fine-grained chalk with planktonic foraminifera, Bed 1+(80), lower part of Louth Member. (D) – Fine-grained chalk with planktonic foraminifera and rare calcispheres, Bed 1+(74), lower part of Louth Member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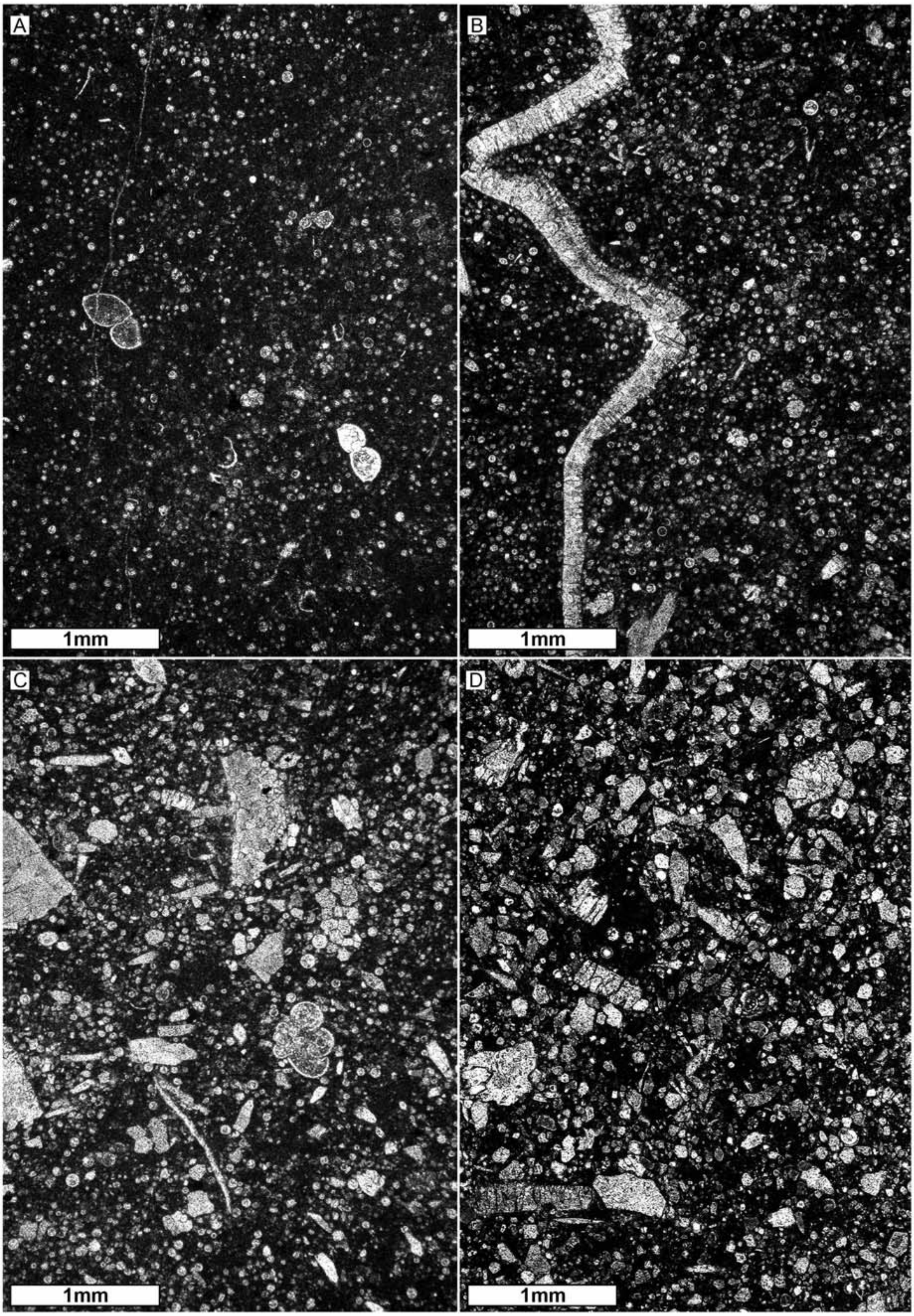
B
0.2mm
C
0.2mm
D
0.2mm


A
1mm
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C
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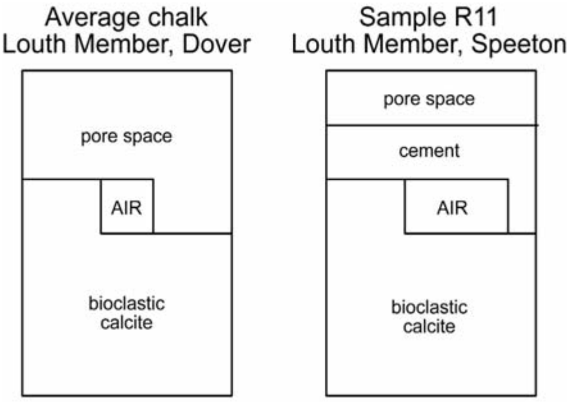
Comparison with Standard Louth Chalk

Average values in Unit A for different localities (Table 3) may differ markedly from the **Standard Louth Chalk** (Table 1). Bulk specific gravity is higher (2.11–2.24 cf. 1.64), $CaCO_3$ contents are generally higher (92–98% cf. 93%), Fe is higher (348–832 ppm cf. 256 ppm), Mn is usually higher (323–771 ppm cf. 331 ppm), Mg is similar (1219–1559 ppm cf. 1303 ppm), Sr is usually lower (445–574 ppm cf. 548 ppm), Oxygen isotope values are generally lower (-2.50 to -4.50‰ cf. -2.84‰), and carbon isotope values tend to be a little higher 2.60–3.18‰ cf. 2.6‰).



Average chalk Louth Member, Dover		Sample R11 Louth Member, Speeton
1.64	specific gravity	2.26
39.5	porosity vol. %	16.3
93.2	$CaCO_3$ wt. %	90.5
56.6	$CaCO_3$ vol. %	75.8
6.8	AIR wt. %	9.5
4.1	AIR vol. %	7.9
255	Fe (calcite) ppm	489
330	Mn (calcite) ppm	575
1312	Mg (calcite) ppm	1835
550	Sr (calcite) ppm	637
-2.84	$\delta^{18}O$ (calcite) ‰	-4.37
2.62	$\delta^{13}C$ (calcite) ‰	3.05

Model cement

cement vol. %	19.1
Fe (calcite) ppm	1183
Mn (calcite) ppm	1301
Mg (calcite) ppm	3385
Sr (calcite) ppm	895
$\delta^{18}O$ (calcite) ‰	-8.91
$\delta^{13}C$ (calcite) ‰	4.33

Text-fig. 10. An example of cement modelling by comparing the trace element concentration, stable isotope values, $CaCO_3$ content and bulk specific gravity of a sample of hard chalk (R11) from Unit A at Speeton with the average chalk (**Standard Louth Chalk**) based on the average values of 8 samples from the Louth Member (Zigzag Chalk Formation) at Dover (Table 1)

Average values for Unit B (Table 4) also differ markedly from the **Standard Louth Chalk** (Table1). Bulk specific gravity is higher (2.21–2.34 cf. 1.64), $CaCO_3$ contents are higher (95–98% cf. 94%), Fe is usually higher (197–672 ppm cf. 256 ppm), Mn is higher (323–503 ppm cf. 331 ppm), Mg is usually higher (1165–3608 ppm cf. 1312 ppm) and Sr is nearly always lower (342–550 ppm cf. 548 ppm). Oxygen isotope values are lower (-3.72 to -4.56‰ cf. -2.84‰). Carbon isotope values are higher (2.85–3.32‰ cf. 2.6‰).

Regional trends in eastern England

The regional patterns in the concentration of trace elements and stable isotopes in the bulk chalk calcite are shown in Text-figs 11A (Fe), 12A (Mn), 13A (Mg), 14A (Sr), 15A ($^{18}O/^{16}O$) and 16A ($^{13}C/^{12}C$). The patterns for Units A and B are very largely independent of each other and are not continuous across the Variegated Beds. In each of the two units the contours of concentration are usually at a high angle to the general direction of bedding as defined by the base of the Variegated Beds or the primary marl seams. The only exception is the Mn pattern (Text-fig. 12A), where there is broad correlation between the bedding direction and the variations in concentration. The regional trends in average values are discussed below.

Unit A: Bulk specific gravities (Table 3) at Welton, South Thoresby, Tetford and Elsham range from 2.11 to 2.17, whereas at Caistor, South Ferriby and Speeton they are higher, ranging from 2.21 to 2.24. The Fe content of the bulk calcite (Table 3; Text-fig. 11A) increases from south Lincolnshire (350–460 ppm) to the north of the county (614–832) and then decreases to the north at Speeton (564 ppm), values are exceptionally low (350–380 ppm) where the Upper Pink Band has not been sulphidized (South Thoresby, Tetford). The Mn content of the bulk calcite (Table 3; Text-fig. 12A) displays particularly low values at South Thoresby (320 ppm) and high values at Speeton (1063 ppm). The Mg content of the bulk calcite (Table 3; Text-fig. 13A) averages 1366 ppm for eastern England with somewhat enhanced values at Caistor (1507 ppm) and Speeton (1559 ppm). The Sr content (Table 3; Text-fig. 14A) averages 522 ppm, values from Wel-

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Text-fig. 9. Micrographs of thin section illustrating the lithofacies of Unit B. (A) – Planktonic foraminifera and abundant calcispheres in a fine-grained chalk matrix. LR353, Elsham. (B) – Compacted fragment of an inoceramid bivalve in a chalk very rich in calcispheres. LR348, Elsham. (C) – Chalk rich in inoceramid bivalve prisms, foraminifera and calcispheres. LR319, Flixton. (D) – Chalk rich in inoceramid bivalve prisms. LR372, Tetford ton, South Thoresby and Tetford are between 445 and 488 ppm, whereas the more northerly locations (Caistor, Elsham, South Ferriby and Speeton) have average values between 518 and 574 ppm. Oxygen isotope values (Table 3; Text-fig. 15A) become lower from the south to the north (-3.30‰ to -4.50‰): Carbon isotope values (Table 3; Text-fig. 16 A) show no obvious regional variation, although Caistor and South Ferriby and Speeton have somewhat higher values ranging from 4.03 to 4.07‰.

Unit B: Bulk specific gravities (Table 4) are generally higher (2.31–2.34) in the northern locations (Caistor, South Ferriby, Flixton) than in the southern ones (2.21–2.29) although Elsham (2.24) belongs to the southern group. The Fe content of the bulk calcite (Table 4; Text-fig. 11A) shows appreciably lower values at Tetford (353 ppm) and Flixton (197 ppm) within a south to north trend of increasing values (487 to 672 ppm). The Mn content of the bulk calcite (Table 4; Text-fig. 12A) varies between 399 and 503 ppm showing no regional trend. The Mg content of the bulk calcite (Table 4; Text-fig. 13A) displays enhanced values in the southern part of the region ranging from 1539 to 1608 ppm compared to 1165 to 1399 at Elsham, South Ferriby and Flixton. The Sr content of the bulk calcite (Table 4; Text-fig. 14A) tends to have higher average values (389−550 ppm) in the north than in the south (342–369 ppm). Oxygen isotope values (Table 4; Text-fig. 15A) display no particular regional trend, whereas carbon isotope values (Table 4: Text-fig. 16A) show a south to north trend of increasingly higher values from 2.85‰ at Welton to ~ 3.30‰ in the north.

Geochemical patterns in model cement

The regional patterns displayed by the trace element and stable isotope values for the model cement (Tables 3, 4) are discussed below.

Fe Pattern (Text-fig. 11B)

Unit A: Model Fe values range from 700 to 2500 ppm. The contoured pattern of regional variation bears no correlation to the overall bedding direction. High values (1400–2500 ppm) are restricted to the northern localities (Caistor, Elsham, South Ferriby, Speeton) whereas lower values (450–1300 ppm) are dominant in the south and these are responsible for the complex pattern of contours centred on South Thoresby. The lowest model Fe values (400–980 ppm) occur at Tetford and South Thoresby in chalk where the Upper Pink Band is preserved.

Unit B: Model Fe values range from -100 to 2380 ppm. The contoured pattern of regional variation consists of two components. At Flixton, the contours representing the rapidly changing values from -100 to 310 ppm may be part of a pattern parallel to the direction of bedding and reflect lithofacies changes. The pattern in Lincolnshire (South Ferriby to Welton) is broad, generally cross-cutting the stratigraphy with lower values in the south (e.g. Tetford). There is an exceptional negative value (-59 ppm, sample LR372) at Tetford in chalk generally characterized by values of 370–450 ppm. At South Ferriby and Elsham there is a thin zone of particularly high Fe content (> 2000 ppm) which includes the Green Trace Bed and is parallel to the general bedding direction. A stratigraphical upwards decrease in model Fe values occurs in Unit B at South Ferriby, Elsham, Caistor, Tetford and Welton.

Mn Pattern (Text-fig. 12B)

Unit A: Model Mn values range from 203 to 3618 ppm. Two main features dominate the contoured pattern of variation. There is a conspicuous zone of high values (>2000 ppm) in the lower part of the sequence that extends from Speeton to Welton. At South Thoresby, exceptional low values (203–271 ppm) result in closely spaced contours that are reflected in the upper part of the Louth Member as far north as South Ferriby and beyond; it also affects the high Mn zone at South Thoresby.

Unit B: Model Mn values range from 260 to 1580 ppm, there is a unique negative value (-73 ppm) from sample LR343 (Green Trace Bed, Elsham). The contoured pattern of variation is subparallel to the stratigraphy although locally it cuts across it; for example, at Elsham relatively low Mn values in the lower part of the sequence result in cross-cutting contours. The section between the top of the Variegated Beds and the base of the Green Trace Bed displays an overall N-S decrease in values from 1016–1579 ppm at Flixton to 589–1191 at Tetford, South Thoresby and Welton. Each section displays an up-sequence decrease of Mn values. The pattern at Flixton is somewhat different because the uppermost part of the sequence displays distinct oscillations between higher (>600 ppm) and lower values (<600 ppm).

Mg Pattern (Text-fig. 13B)

Unit A: Model Mg values range from 636 to 3345 ppm. The contoured pattern of regional variation bears no correlation to the overall bedding direction. High Mg values are restricted to Speeton (>3000 ppm) and

Calcite trace elements, stable isotopes and model cements in Unit A, Louth Member (Ferriby Formation), eastern England

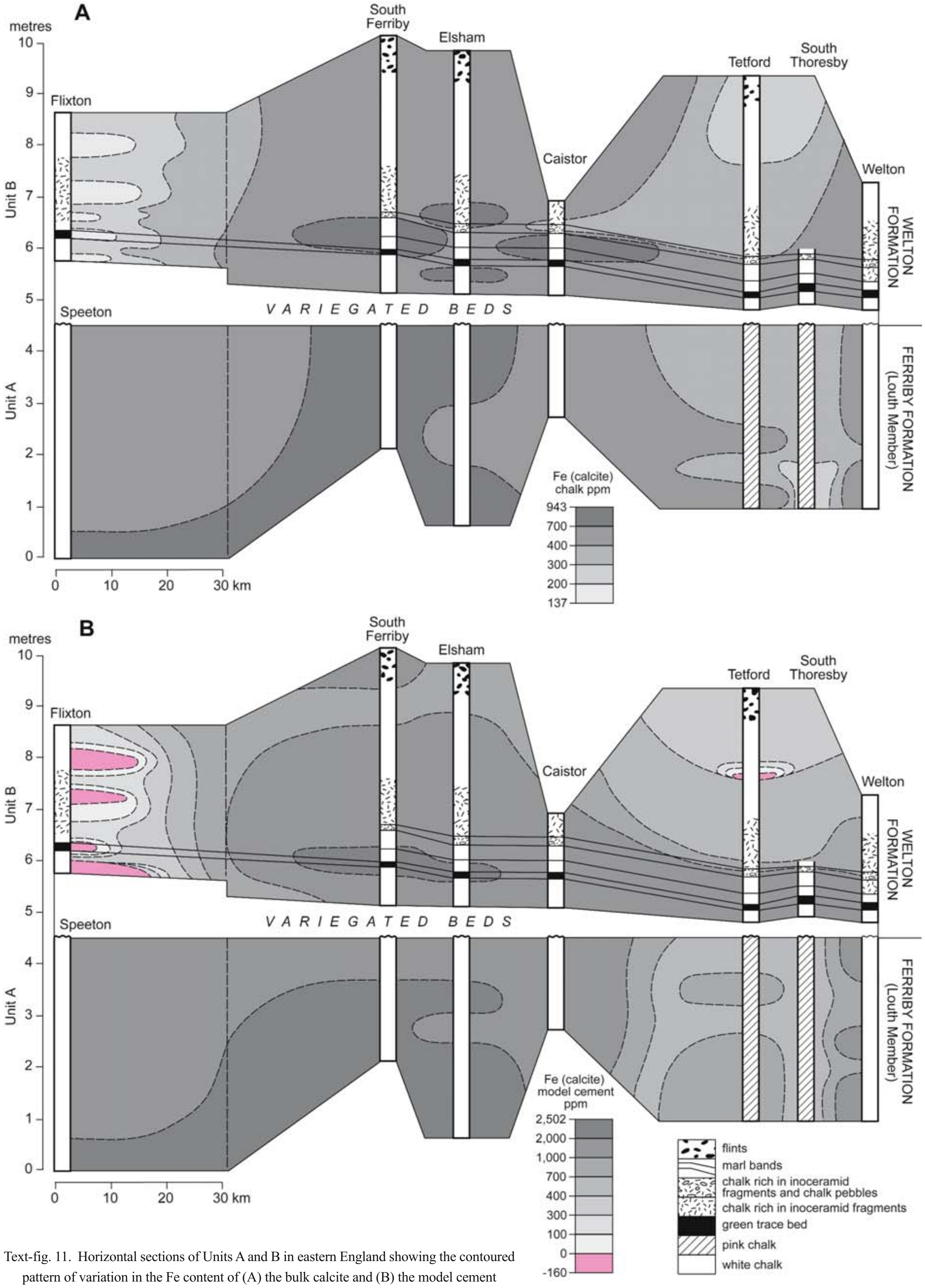
Sample No.	$CaCO_3$ wt%	SG	Fe (calcite) ppm	model	Mn (calcite) ppm	model	Mg (calcite) ppm	model	Sr (calcite) ppm	model	$\delta^{18}O_{VPDB}$ ‰	model	$\delta^{13}C_{VPDB}$ ‰	model
WELTON														
LR392	99	2.24	491	1015	420	620	1352	1441	457	250	-3.24	-4.13	2.94	3.65
LR391	99	2.14	483	175	375	492	1394	1607	41	216	-3.17	-4.03	3.03	4.09
LR382	97	2.17	455	986	350	403	1422	1714	449	181	-3.27	-4.41	2.96	3.86
LR383	98	2.14	445	957	340	147	1399	1634	445	162	-3.18	-4.10	2.94	3.21
LR384	97	2.18	444	938	334	344	1353	1460	461	228	-3.17	-4.03	2.91	3.67
LR385	98	2.06	455	1080	371	499	1303	1275	473	233	-3.30	-4.74	2.89	3.05
LR386	97	2.09	467	1118	440	782	1258	1092	483	277	-3.29	-4.67	2.99	4.13
LR387	95	2.03	370	810	418	755	1172	636	482	222	-3.24	-4.77	2.86	3.78
LR388	98	2.06	471	1146	778	2178	1247	1044	518	418	-3.30	-4.74	2.79	3.32
LR389	96	2.03	467	1240	695	2025	1146	541	548	541	-3.45	-5.67	2.84	3.64
LR390	97	2.04	488	1281	1027	3398	1160	643	580	682	-3.74	-6.80	2.84	3.59
range	95~99	2.03~2.24	370~491	810~1281	334~1027	147~3398	1146~1422	541~1714	445~580	162~682	-3.74 to -3.17	-6.80 to -4.03	2.79~3.03	3.05~4.13
average	97	2.11	458	977	504	1058	1291	1190	449	310	-3.30	-4.74	2.91	3.64
SOUTH THORESBY														
LR354	99	2.28	389	671	311	271	1513	1935	428	172	-3.54	-5.01	2.93	3.58
LR355	99	na	356	594	309	260	1400	1607	435	164	-3.62	-5.46	2.92	3.63
LR356	98	2.22	376	653	304	245	1428	1693	433	172	-3.52	-5.08	2.88	2.83
LR357	97	2.11	324	622	298	203	1316	1328	472	242	-3.41	-5.09	2.98	4.04
LR358	99	2.07	293	405	391	570	1159	709	459	191	-3.42	-5.13	2.75	3.13
range	97~99	2.07~2.28	293~389	405~671	298~391	203~570	1159~1513	709~1935	428~472	164~242	-3.62 to -3.41	-5.46 to -5.01	2.75~2.98	2.83~4.04
average	98	2.17	348	589	323	310	1363	1454	445	188	-3.50	-5.08	2.89	3.44
TETFORD														
LR376	99	2.23	313	444	336	350	1318	1332	426	147	-3.86	-6.16	2.01	0.64
LR377	98	2.17	384	714	343	376	1412	1668	463	240	-3.83	-6.37	2.61	2.58
LR378	98	2.14	353	617	319	289	1404	1652	428	99	-3.51	-5.32	2.25	1.25
LR379	97	2.06	410	915	494	129	1409	1725	462	175	-3.42	-5.31	3.00	3.52
LR380	96	2.09	392	831	800	2307	1316	1329	501	344	-3.56	-5.87	2.78	3.29
LR381	96	2.05	416	977	843	2631	1182	729	563	608	-3.66	-6.52	2.95	4.10
range	96~99	2.05~2.23	313~416	444~977	319~843	129~2631	1182~1412	729~1725	426~563	99~608	-3.86 to -3.42	-6.52 to -5.31	2.01~3.00	0.64~4.10
average	97	2.12	378	750	523	1014	1340	1406	474	269	-3.64	-5.93	2.60	2.56
CAISTOR														
LR400	96	2.19	600	1513	487	902	1569	2245	588	689	-3.83	-6.45	3.14	4.52
LR401	98	2.24	579	1323	471	795	1493	1909	552	557	-3.44	-4.82	3.10	4.20
LR402	100	2.23	621	1420	512	909	1533	2015	537	509	-3.71	-5.01	3.08	3.60
LR403	98	2.19	636	1580	515	974	1562	2182	555	567	-3.60	-5.48	3.00	3.94
LR404	97	2.2	635	1604	529	1036	1380	1553	618	791	–	–	–	–
range	96~100	2.19~2.24	579~636	1323~1604	471~529	795~1036	1380~1568	1553~2245	537~618	509~791	-3.44 to -3.83	-6.45 to - 4.82	3.00~3.14	3.60~4.52
average	98	2.21	614	1488	503	923	1507	1981	570	623	-3.65	-5.44	3.08	4.07
ELSHAM														
LR342	99	2.31	755	1764	439	659	1268	1179	514	441	-4.01	-6.67	2.22	1.41
LR341	99	2.16	773	2084	463	800	1329	1372	519	441	-3.66	-5,.74	2.83	3.36
LR340	100	2.09	642	1697	483	900	1242	1051	490	326	-3.66	-5.90	2.78	3.22
LR339a	94	2.04	639	2152	509	1214	1157	546	515	377	-3.62	-6.69	2.85	3.76
LR338a	96	2.07	733	2329	670	1805	1154	626	523	433	-3.71	-6.62	2.89	3.79
LR337a	96	2.05	756	2502	1063	3618	1168		544	523	-3.75	-6.92	2.82	3.52
range	94~100	2.04~2.31	639~773	1697~2502	439~1063	659~3618	1154~1329	546~1372	490~544	326~441	-4.01 to -3.62	-6.92 to -5.74	2.22~2.89	1.41~3.79
average	97	2.12	716	2088	605	1499	1220	955	518	424	-3.74	-6.42	2.73	3.18
SOUTH FERRIBY														
LR334	97	2.28	792	1996	436	674	1277	1199	514	433	-4.20	-7.25	3.11	4.21
LR335	98	2.26	874	2255	457	740	1366	1486	547	540	-4.16	-7.11	3.12	4.24
LR336	96	2.17	830	2417	559	1191	1277	1180	512	407	-4.11	-7.62	2.98	3.97
range	96~98	2.17~2.28	792~874	1996~2417	436~559	674~1191	1277~1366	1180~1486	512~547	407~540	-4.20 to -4.11	-7.62 to -7.11	2.98~3.12	3.97~4.24
average	97	2.24	832	2223	484	868	1307	1288	524	460	-4.16	-7.33	3.07	4.14
SPEETON														
R11	91	2.26	489	1183	575	1301	1835	3385	637	895	-4.37	-8.91	3.05	4.33
R12	90	2.24	503	1277	574	1336	1805	3344	626	1146	-4.3	-8.86	2.99	4.15
R13	90	2.19	545	1564	548	1314	1726	3181	668	1083	-4.35	-9.66	2.95	4.11
R4	92	2.24	520	1283	779	1121	1324	1359	445	143	-4.6	-9.67	3.02	4.17
R3	99	2.27	588	1297	850	1958	1275	1196	430	174	-4.69	-8.63	2.94	3.62
R2	92	2.25	590	1538	1159	3504	1199	879	512	404	-4.75	-10.15	2.92	3.77
R10	88	2.22	710	2377	910	3058	1748	3345	702	1259	-4.58	-7.92	2.93	4.07
range	88-99	2.19-2.27	489-710	1183-2377	548-1159	1121-3504	1199-1835	879-3385	512-702	143-1259	-4.3 to'-4.75	-7.92 to -10.15	2.92-3.05	3.62-4.33
average	92	2.24	564	1503	771	1942	1559	2384	574	715	-4.52	-9.11	2.97	4.03

Table 3. $CaCO_3$ contents, bulk specific gravity, acid insoluble residues, trace element concentration and stable isotope values in the bulk calcite and the model trace element and stable isotope values for samples from Unit A, Ferriby Formation, eastern England

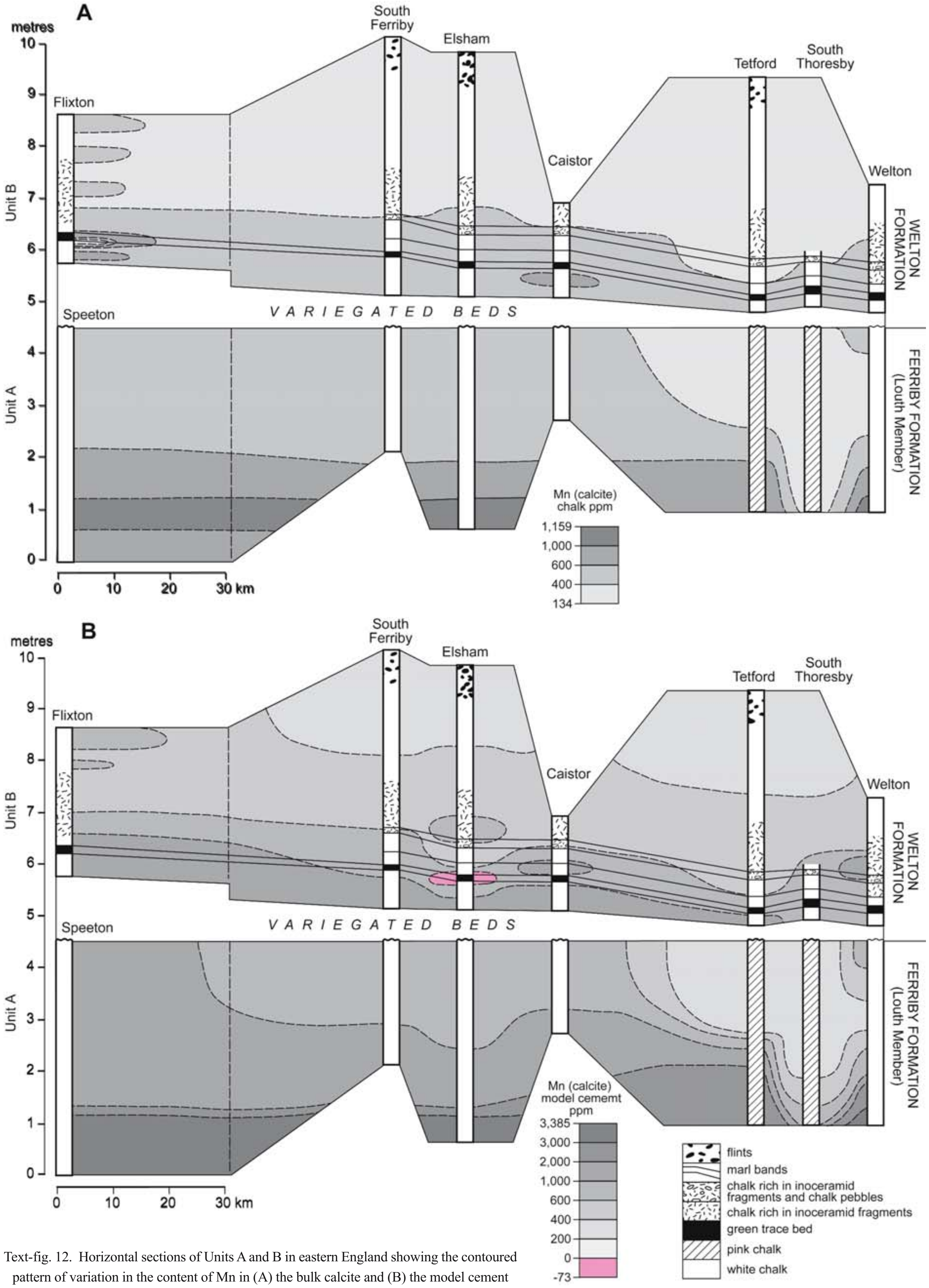
Calcite trace elements, stable isotopes and model cements in Unit B, Welton Formation , eastern England

Sample No.	$CaCO_3$ wt%	SG	Fe (calcite) ppm	model	Mn (calcite) ppm	model	Mg (calcite) ppm	model	Sr (calcite) ppm	model	$\delta^{18}O_{VPDB}$ ‰	model	$\delta^{13}C_{VPDB}$ ‰	model
WELTON														
LR399	99	2.33	402	691	388	502	1734	2564	310	-162	-3.94	-6.10	2.68	2.80
LR398	99	2.30	463	888	389	510	1620	2250	319	-154	-4.07	-6.59	2.72	2.92
LR397	99	2.34	437	791	399	533	1622	2224	322	-121	-4.52	-7.78	2.54	2.38
LR396	98	2.33	472	912	462	1399	1573	2102	319	-162	-3.92	-6.11	2.89	3.44
LR395	100	2.31	597	1267	475	759	1682	2407	328	-107	-3.74	-5.50	3.04	3.86
LR394	98	-	540	-	490	-	1550	-	362	-	-3.75	-	3.09	-
LR393	96	2.15	501	1204	497	975	1272	1158	466	226	-4.35	-8.67	2.98	4.01
range	96~100	2.15~2.34	402~597	691~1267	388~497	502~1399	1272~1734	1158~2564	310~3185	-162~226	-4.52 to -3.74	-8.67 to -5.5	2.54~3.09	4.01~3.86
average	98	2.29	487	959	443	780	1579	2118	347	-80	-4.04	-6.79	2.85	1.90
SOUTH THORESBY														
LR362	99	2.37	533	1053	443	655	1721	2487	325	-96	-4.18	-6.69	2.95	2.79
LR361	98	2.28	539	1155	507	891	1688	2503	354	-71	-4.13	-6.93	2.87	3.41
LR360	97	2.16	501	1177	444	994	1522	2099	392	-42	-3.89	-6.78	3.17	4.68
LR359	99	2.15	440	912	403	589	1223	996	405	35	-4.61	-9.13	2.68	2.83
range	97~99	2.15~2.37	440~539	912~1177	403~507	589~994	1223~1721	996~2503	325~405	-96~35	-4.61 to -3.89	-9.13 to -6.69	2.68~2.95	2.79~4.68
average	98	2.24	503	1074	449	782	1539	2021	369	-44	-4.20	-7.38	2.83	3.43
TETFORD														
LR375	99	2.24	296	387	325	314	1468	1815	364	-74	-4.19	-7.19	2.50	2.23
LR374	99	2.24	293	377	313	275	1606	2259	337	-125	-4.10	-6.90	2.62	2.62
LR372	96	2.12	177	-59	343	382	1736	3018	293	-484	-2.86	-2.95	3.06	4.39
LR373	99	2.22	316	456	340	363	1662	1364	347	-117	-3.93	-6.42	2.79	3.18
LR371	100	2.29	353	550	393	520	1593	2158	303	-194	-4.02	-6.39	2.89	3.43
LR370	99	2.32	352	551	397	535	1636	2302	309	-186	-3.77	-5.68	3.17	4.30
LR369	99	2.30	506	1019	398	537	1641	2314	349	-82	-3.91	-6.10	3.24	4.51
LR368	89	2.11	178	-160	418	804	1647	3117	289	-856	-2.69	-2.03	3.42	6.93
LR367	98	2.23	498	1064	461	766	1543	2081	366	-63	-3.93	-6.47	3.25	4.72
LR366	98	2.10	458	1018	467	863	1412	1702	392	-65	-4.09	-7.71	3.16	4.72
LR364	96	2.10	458	1096	538	1191	1367	1540	410	-30	-4.09	-8.02	3.18	4.94
range	89~100	2.1~2.32	177~506	-160~1096	313~538	275~1191	1367~1736	1364~3117	289~410	-856~-30	-4.19 to -2.69	-8.02 to -2.03	2.50~3.42	2.23~6.93
average	97	2.21	353	573	399	595	1574	2152	342	-207	-3.78	-5.99	3.03	4.18
CAISTOR														
LR409	99	2.39	578	1168	381	474	1702	2415	395	112	-3.73	-5.36	3.33	4.63
LR410	94	2.44	398	684	427	621	1881	2809	366	-2	-3.12	-3.68	3.29	4.63
LR408	93	2.38	736	1818	461	756	1846	3048	417	118	-3.91	-6.32	3.17	4.41
LR407	98	2.38	738	1757	570	1076	1621	2273	431	180	-4.48	-7.94	2.97	3.71
LR405	96	2.23	650	1638	472	827	1514	2019	491	343	-4.38	-8.23	3.15	4.48
LR406	96	2.30	640	1507	627	1296	1457	1784	503	397	-4.36	-7.79	3.02	3.92
LR411	89	2.27	666	1946	584	1375	1238	1008	552	558	-4.60	-10.08	3.20	5.01
range	89~99	2.23~2.44	398~738	684~1946	381~627	474~1375	1238~1881	1008~3048	366~552	-2~558	-4.48 to -3.12	-10.08 to -3.68	2.97~3.33	3.71~5.01
average	95	2.34	629	1503	503	918	1608	2194	451	244	-4.08	-7.06	3.16	4.40
ELSHAM														
LR353	99	2.28	-	-	-	-	-	-	-	-	-4.01	-6.47	3.30	4.73
LR352	99	2.29	489	974	307	259	1324	1349	469	301	-1.18	-6.96	3.17	4.31
LR351	100	2.37	593	1208	346	375	1574	2051	378	65	-4.07	-6.31	2.95	3.55
LR350	98	2.27	515	1087	353	404	1498	1907	329	-157	-3.34	-4.44	3.12	4.22
LR349	99	2.36	596	1242	386	492	1539	1969	328	-93	-3.74	-5.45	3.03	3.81
LR348	100	2.32	682	1508	395	521	1514	1905	348	-43	-3.82	-5.72	3.18	4.26
LR345	98	2.32	758	1791	448	690	1438	1697	380	31	-3.91	-6.11	3.13	4.18
LR344	98	2.18	670	1715	406	597	1375	1534	386	-27	-4.13	-7.38	3.02	4.03
LR343	97	1.98	687	2376	423	-73	1265	1081	400	-186	-3.99	-8.49	3.17	5.32
LR346	98	2.18	706	1842	483	868	1129	668	425	181	-4.41	-8.36	3.00	3.96
LR347	94	2.07	537	1572	499	1119	917	-533	445	60	-4.32	-9.75	3.10	4.86
range	94~100	1.98~2.37	489~758	974~2376	307~499	-73~1119	917~1574	-533~2051	328~469	-186~301	-4.41 to -1.18	-9.75 to -4.44	2.95~3.30	3.55~5.32
average	98	2.24	623	1532	405	525	1357	1363	389	13	-3.72	-6.86	3.11	4.29
SOUTH FERRIBY														
LR333	99	2.34	514	1016	329	327	1420	1628	474	326	-4.73	-8.39	3.34	4.73
LR332	98	2.30	489	986	329	327	1496	1723	403	91	-4.55	-8.18	3.29	4.71
LR331	99	2.29	619	1373	339	358	1529	1979	396	77	-4.39	-7.60	3.30	4.71
LR330	100	2.37	587	1191	365	429	1546	1972	351	-11	-4.23	-6.76	3.26	4.42
LR328	100	2.34	648	1389	362	422	1547	1990	399	114	-4.62	-7.98	3.40	4.87
LR329	99	2.30	633	1406	366	440	1612	2226	382	38	-4.62	-8.26	3.24	4.51
LR327	100	2.41	880	1965	452	664	1506	1843	368	52	-4.32	-6.89	3.25	4.34
LR326	99	2.35	943	2262	494	809	1529	1945	397	104	-4.38	-7.33	3.38	4.84
LR325	98	2.23	829	2167	467	786	1420	1672	432	157	-4.58	-8.64	3.19	4.52
LR337	88	2.27	635	1876	507	1085	983	-91	391	-128	-4.67	-10.64	3.18	5.01
LR338	87	-	613	1842	505	1106	801	-953	387	-173	-5.06	-12.68	3.28	5.55
range	87~100	2.23~2.41	489~943	986~2262	329~507	327~1106	801~1612	-953~2226	351~474	-173~326	-5.06 to -4.23	-12.68 to -6.76	3.24~3.40	4.34~5.55
average	97	2.32	672	1588	410	614	1399	1449	398	59	-4.56	-8.49	3.32	4.75
FLIXTON														
LR322	97	2.36	230	180	450	691	1313	1315	457	270	-3.78	-5.67	3.29	4.64
LR320	97	2.34	137	-107	374	645	1308	1300	449	240	-3.69	-5.45	3.24	4.52
LR319	96	2.40	148	-64	422	604	1401	1577	424	175	-3.16	-3.79	3.27	4.55
LR318	96	2.37	142	-90	406	562	1321	1339	439	211	-3.01	-3.36	3.24	4.51
LR317	97	2.40	202	101	384	487	1286	1236	464	299	-3.83	-5.73	3.39	4.86
LR316	98	2.47	159	-6	405	534	1392	1529	421	200	-3.68	-5.12	3.34	4.58
LR315	99	-	184	-	387	-	1442	-	457	-	-3.84	-	3.26	-
LR314	91	2.43	203	86	790	851	1537	2045	439	188	-3.54	-5.12	3.33	4.93
LR313	94	2.38	236	195	453	719	1453	1758	426	158	-3.68	-5.50	3.25	4.61
LR311	96	-	177	-	428	-	1260	-	451	-	-3.95	-	3.13	-
LR310	95	2.39	238	203	595	1142	1187	929	450	244	-3.76	-5.66	3.18	4.34
LR309	95	2.39	175	9	608	1185	1290	1244	511	430	-3.97	-6.32	3.21	4.44
LR308	95	2.31	171	-22	598	1214	1281	1210	529	481	-4.00	-6.67	3.25	4.70
Ysa98	91	-	207	-	134	-	727	-	716	-	-6.73	-	3.55	-
LR307	93	-	264	-	493	-	915	-	957	-	-5.37	-	3.25	-
LR306	96	2.19	205	-72	517	1106	741	-782	703	1111	-5.47	-12.49	3.08	4.31
LR304	94	2.11	268	312	616	1579	829	-797	696	1188	-5.21	-13.19	3.10	4.72
LR305	92	2.08	186	-89	551	1431	734	-1567	712	1357	-5.42	-21.06	3.11	5.06
LR303	89	2.04	208	-43	496	1383	719	-2450	742	1768	-5.82	-21.74	3.32	7.06
range	89~99	2.04~2.47	137~268	-107~312	134~790	487~1579	719~1537	-2450~2045	421~957	158~1768	-6.73 to -3.01	-21.74 to -3.36	3.08~3.55	4.31~7.06
average	95	2.31	197	40	479	942	1165	659	550	555	-4.31	-8.46	3.25	4.21

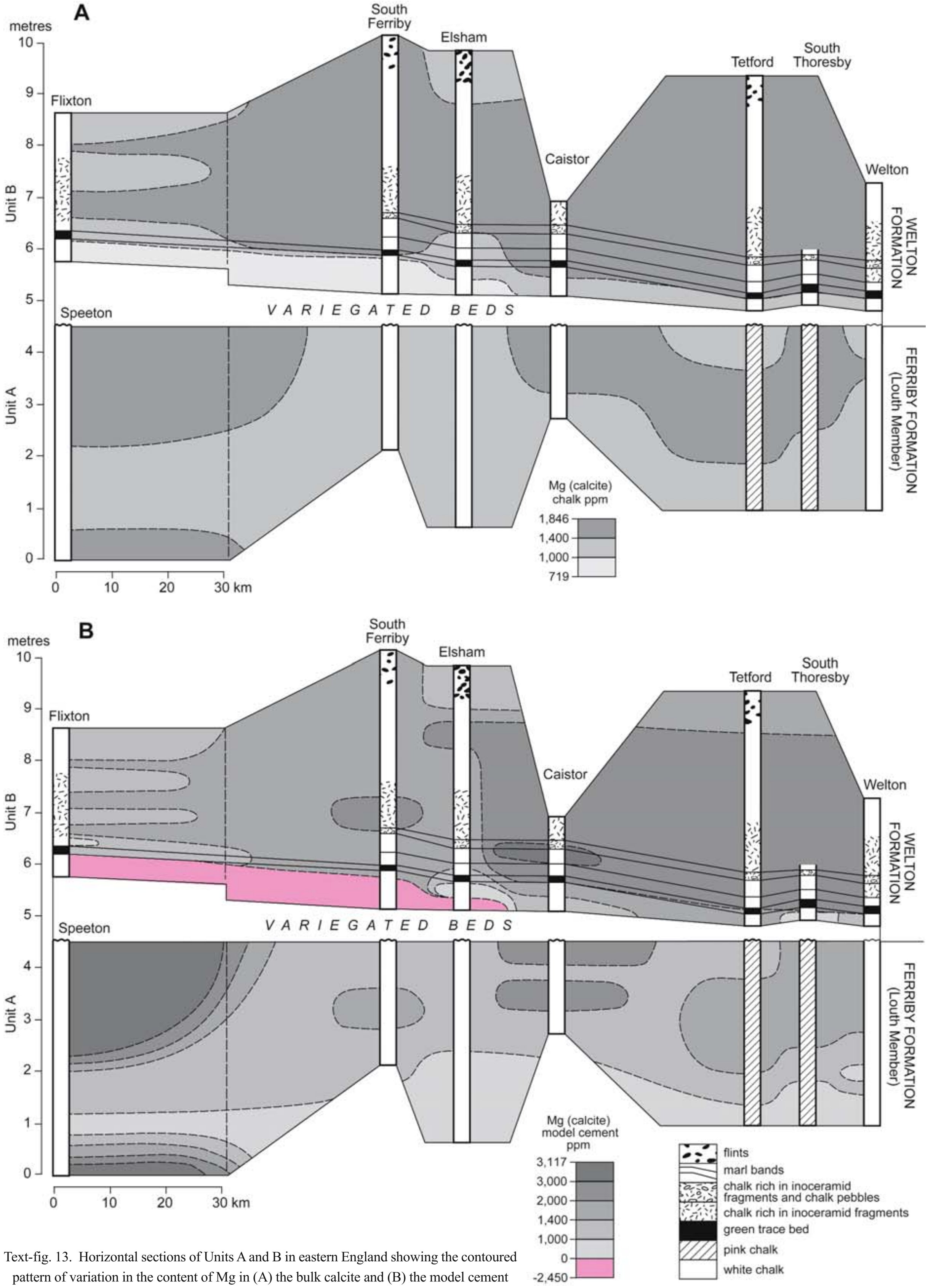
Table 4**.** $CaCO_3$ contents, bulk specific gravity, acid insoluble residues, trace element concentration and stable isotope values in the bulk calcite and the model trace element and stable isotope values for samples from Unit B, Welton Formation, eastern England



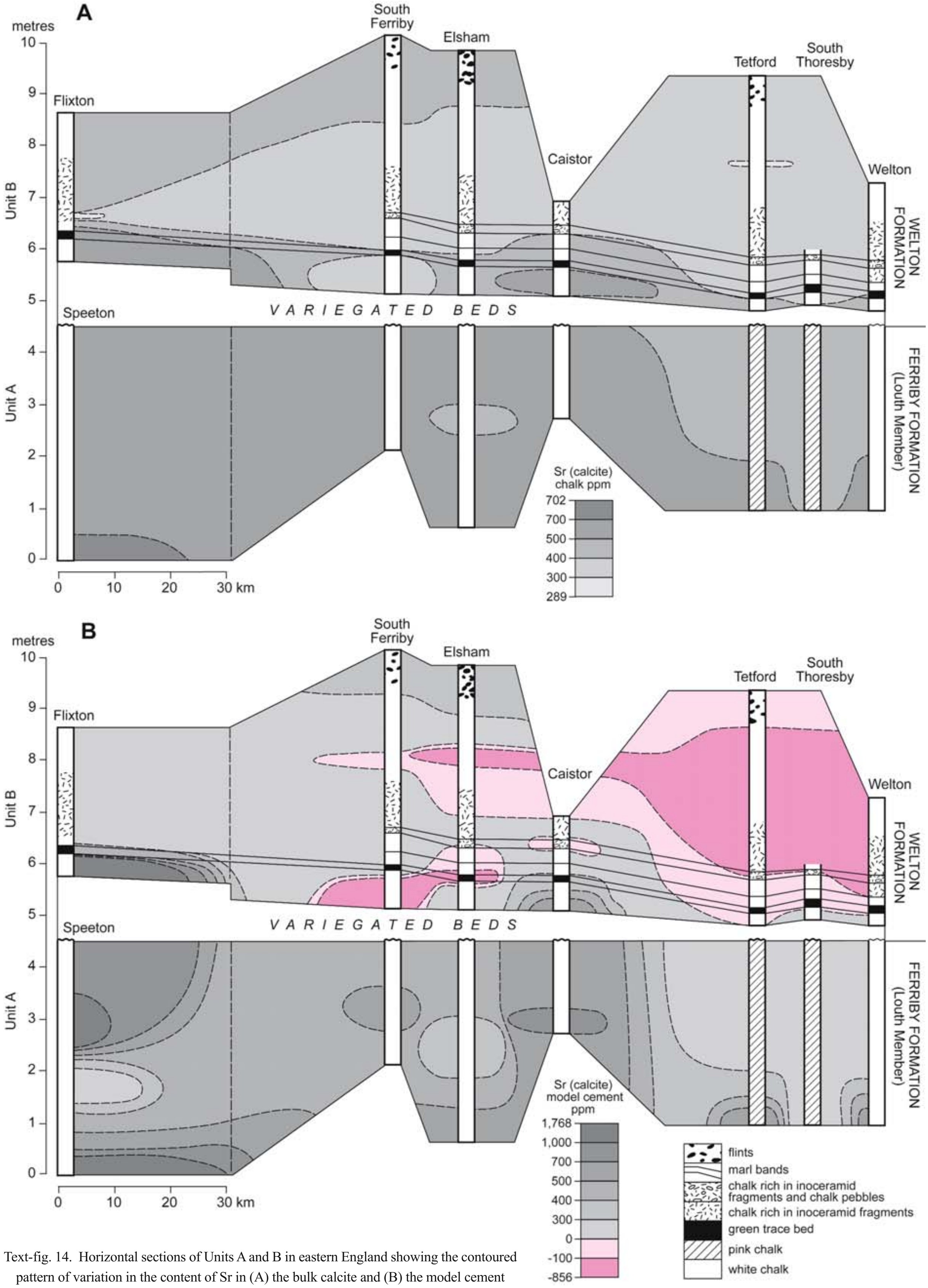
Text-fig. 11. Horizontal sections of Units A and B in eastern England showing the contoured pattern of variation in the Fe content of (A) the bulk calcite and (B) the model cement



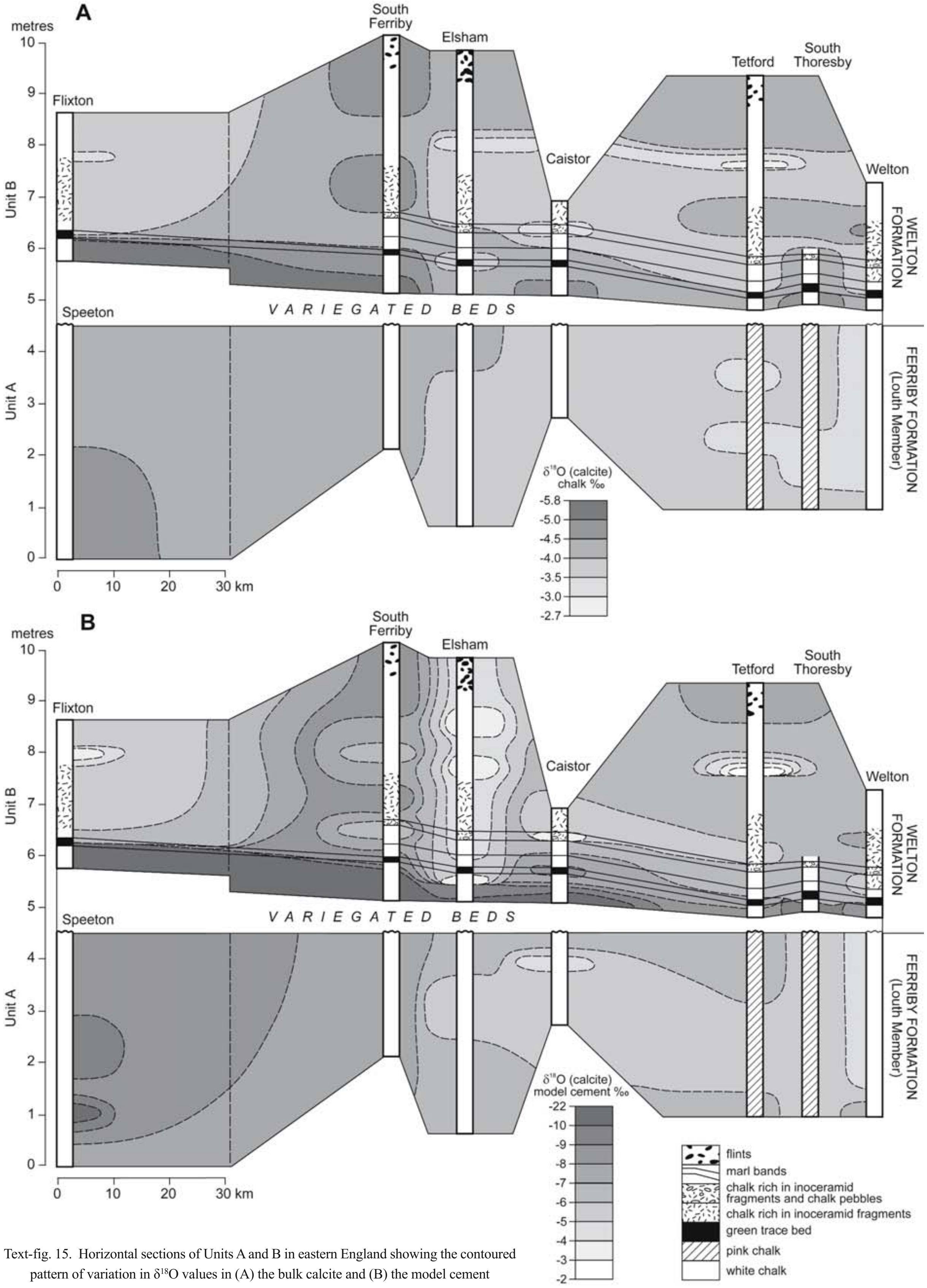
Text-fig. 12. Horizontal sections of Units A and B in eastern England showing the contoured pattern of variation in the content of Mn in (A) the bulk calcite and (B) the model cement



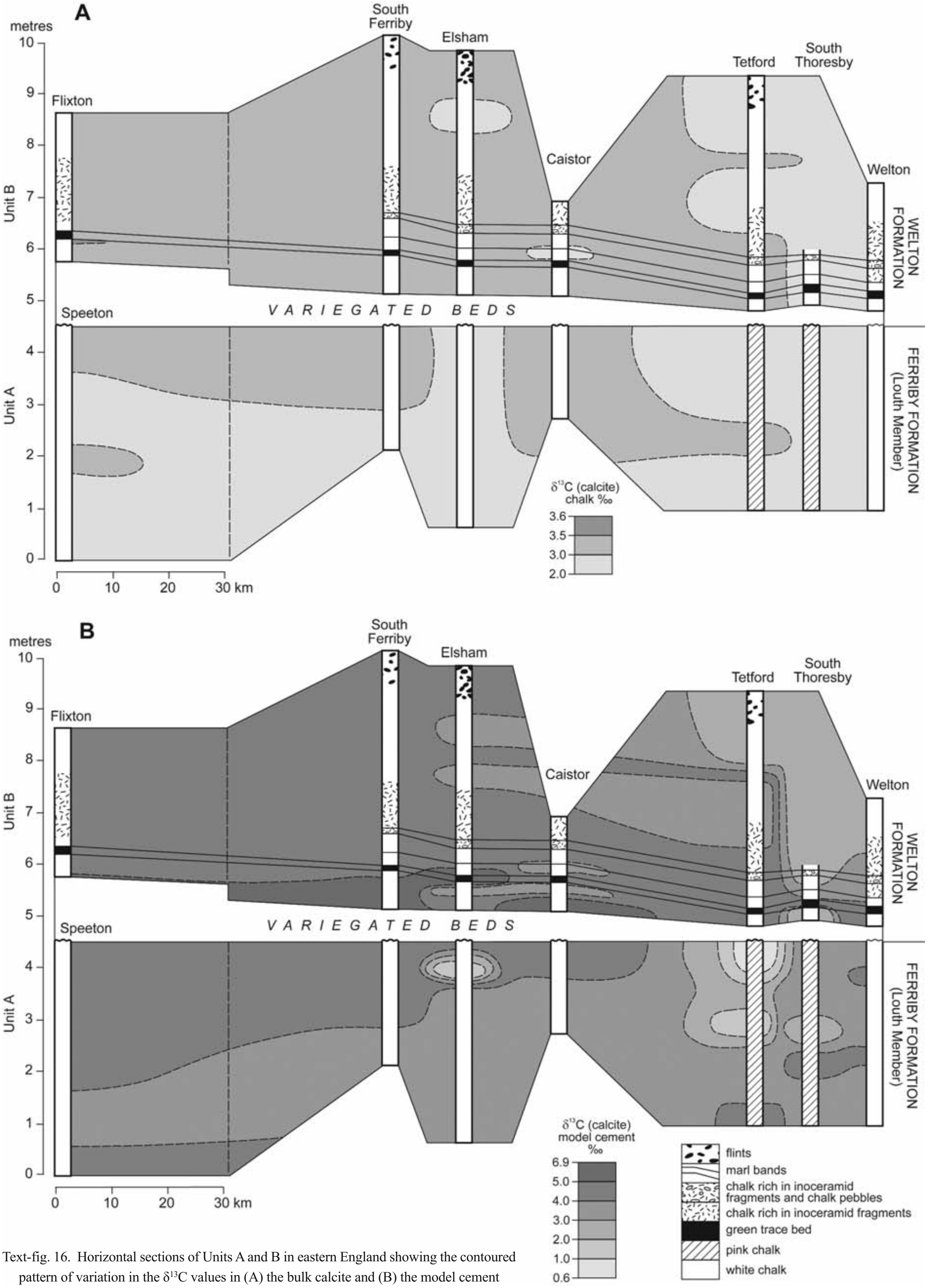
Text-fig. 13. Horizontal sections of Units A and B in eastern England showing the contoured pattern of variation in the content of Mg in (A) the bulk calcite and (B) the model cement



Text-fig. 14. Horizontal sections of Units A and B in eastern England showing the contoured pattern of variation in the content of Sr in (A) the bulk calcite and (B) the model cement



Text-fig. 15. Horizontal sections of Units A and B in eastern England showing the contoured pattern of variation in $\delta^{18}O$ values in (A) the bulk calcite and (B) the model cement



Text-fig. 16. Horizontal sections of Units A and B in eastern England showing the contoured pattern of variation in the δ13C values in (A) the bulk calcite and (B) the model cement

Caistor (>2000 ppm). Low values (<2000 ppm) occur at South Ferriby, Elsham, Tetford, South Thoresby and Welton.

Unit B: Model Mg values range from -2450 to 3018 ppm. The contoured pattern of regional variation bears little obvious correlation to the overall bedding direction. At Flixton between the base of the section and the Green Trace Bed Mg values are very negative (-780 to -2450 ppm). At this level negative values occur also at South Ferriby (-91 ppm) and Elsham (-533 ppm) but these are replaced by positive values at Caistor (1008–1784 ppm), Tetford (1540 ppm), South Thoresby (996 ppm) and Welton (1158 ppm). At Flixton there is an upsequence decrease in the model Mg value in the chalk above the Green Trace Bed that may suggest stratigraphical control. Dominating the sections at Welton, South Thoresby and Tetford and extending to Elsham is an extensive chalk body with high Mg values (≥2000 ppm) defined by the 2000 ppm contour. Its upper and lower limits are approximately parallel to the overall bedding direction. Lithologically it is dominated by chalk rich in Inoceramid fragments and calcispheres (Text-fig. 5).

Sr Pattern (Text-fig.14B)

Unit A: Model Sr values range from 99 to 1260 ppm. The contoured pattern of regional variation bears no correlation to the overall bedding direction. The pattern is dominated by two chalk bodies of low Sr cement – a northern one defined by the 500 ppm contour, this stretches from Speeton with the lowest Sr values (143–174 ppm) to South Ferriby and Elsham; a southern one defined by the 300 ppm contour that includes most of the sections at Tetford with the lowest value (99 ppm), South Thoresby and Welton.

Unit B: Model Sr values range from -484 to 1768 ppm. The contoured pattern of regional variation (Text-fig. 14B) is dominated by an extensive chalk body with negative values, defined by the 0 ppm contour. This includes all or most of the sections at Welton, South Thoresby and Tetford. The chalk body stretches northwards as far as South Ferriby, where it is represented by a single sample (Table 4, LR330, Sr -11 ppm). Small outliers of this zone of negative Sr values occur at Caistor, Elsham and South Ferriby. At Flixton there is an upward decrease in Sr contents; values are particularly high between the base of the section and the Green Trace Bed, ranging between 1117 and 1768 ppm. The cement of the Green Trace Bed has values of 430 to 480 ppm, and the overlying chalk has a Sr content ranging from 158 to 299 ppm. The high Sr cement near the base of the sections at Caistor (558 ppm) and Welton (226 ppm) may be local representatives of the high Sr zone at Flixton. There is a marked increase in Sr contents at the top of section at South Ferriby and Elsham with values going from below 100 ppm to 300 ppm.

δ^{18}O Pattern (Text-fig. 15B)

Unit A: Model δ^{18}O values range from -4‰ to -10‰ , with the more positive values dominating at Welton and the more negative values at Speeton. The pattern of variation is unrelated to bedding with contours often intersecting the base of the Variegated Beds at steep angles. The pattern suggests gradually laterally-increasingly high δ^{18}O values from north to south through the chalk.

Unit B: Model δ^{18}O values range from -2.92‰ to -21.74‰. The overall pattern of variation can be considered to consist of two components, one parallel or subparallel to the primary marl seams, the other is at a high angle to the general bedding. Particularly pronounced are the isotopically light values and lateral variation in the chalk between the top of the Variegated Beds and the base of the Green Trace Bed. At Flixton, these range from -12 to -22‰. They display increasingly less negative values to the south, -9 to -10‰ at South Ferriby, Elsham and Caistor, and -8 to -9‰ at Tetford, South Thoresby and Welton. The more massive chalks overlying the Green Trace Bed display a different regional pattern. At Flixton values range from -3.3‰ to -5.7‰; these become lower when traced southwards, at South Ferriby values range from -6.7 to -8.4‰, at Caistor, Tetford and Welton values generally range from -5.4 to -7.8‰ with a single sample at Tetford having a value of -2.92‰ . Values at Elsham are relatively high, ranging from -3.6‰ to -4.3‰.

δ^{13}C Pattern (Text-fig. 16B)

Unit A: Model δ^{13}C values range from 1.41 to 4.52‰. There is a general decrease in values from Speeton to Caistor, with the 4‰ contour intersecting the base of the Welton Formation between Caistor and Tetford. South of this, at Tetford and South Thoresby, values are generally lower and much more variable (0.64–4.1‰), resulting in a complex of contours. This gives way between South Thoresby and Welton to a simpler pattern dominated by 3.0–4.0‰ values. An exceptional low value (1.41‰) at the top of the sequence at Elsham results in a local nest of contours.

Unit B: Model values range from 2.23 (Tetford) to 7.06‰ (Flixton). There is a general southward decrease in values. Two subsidiary patterns are recognised: (1) the chalks below the Green Trace Bed tend to have the highest values of δ^{13}C which decrease from north to south, and (2) the chalk above the Green Trace Bed displays a gradual replacement of the high δ^{13}C values (≥4‰) of Flixton and South Ferriby with values of <3‰ in the more southern locations. Contours tend to be subparallel to the stratigraphical framework although between Tetford and Welton, rapid changes in values result in a complex pattern.

DETAILED INTERPRETATION

The general occurrence of relatively high model trace element values in Unit A compared to the bulk values leaves little doubt that the **pore-space loss** is due to the precipitation of a cement often with higher trace element values than the bulk hard chalk — and not to the loss of porosity by the improved packing of the original grains as a result of their pressure dissolution or crushing. The pattern of model stable isotope values provides additional support. The oxygen isotope values (-4.03 to -10.15‰) indicate increasing temperatures well above the average for the soft **Standard Louth Chalk** (-2.84‰). The range of model carbon isotope values is similar to those reported by Hu *et al.* (2012) from calcite cements precipitated from the early to the late stages of Chalk diagenesis in eastern England.

The more complicated patterns of model trace element and stable isotope values in Unit B shows the same fundamental differences when compared to the actual values of the hard chalk. This suggests that the **pore-space loss** is again due to a cement with isotope values that indicate its precipitation over a range of temperatures and at stages of diagenesis comparable to those described by Hu *et al.* (2012). The explanation of the negative values of the model trace elements in Unit B is dealt with later.

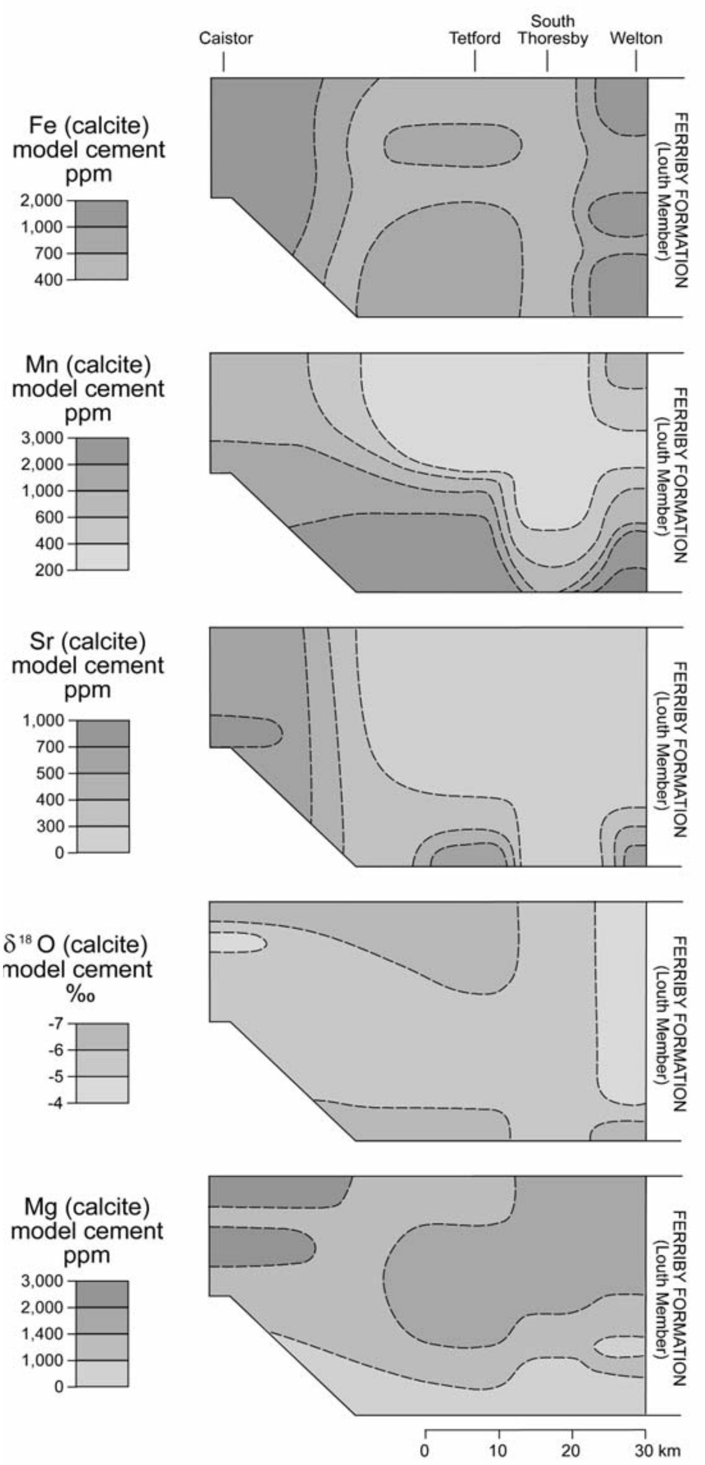
Unit A

The convoluted pattern of contours displayed by the trace element and stable isotope values (Text-figs 11B to 16B) of the model cement show little or no relationship to the regional bedding as defined by the base of the Variegated Beds. This suggests that the precipitation of cement took place from pore fluids that were circulating within Unit A in the uppermost part of the Louth Member as has been suggested by Hu *et al.* (2012, text-fig. 26).

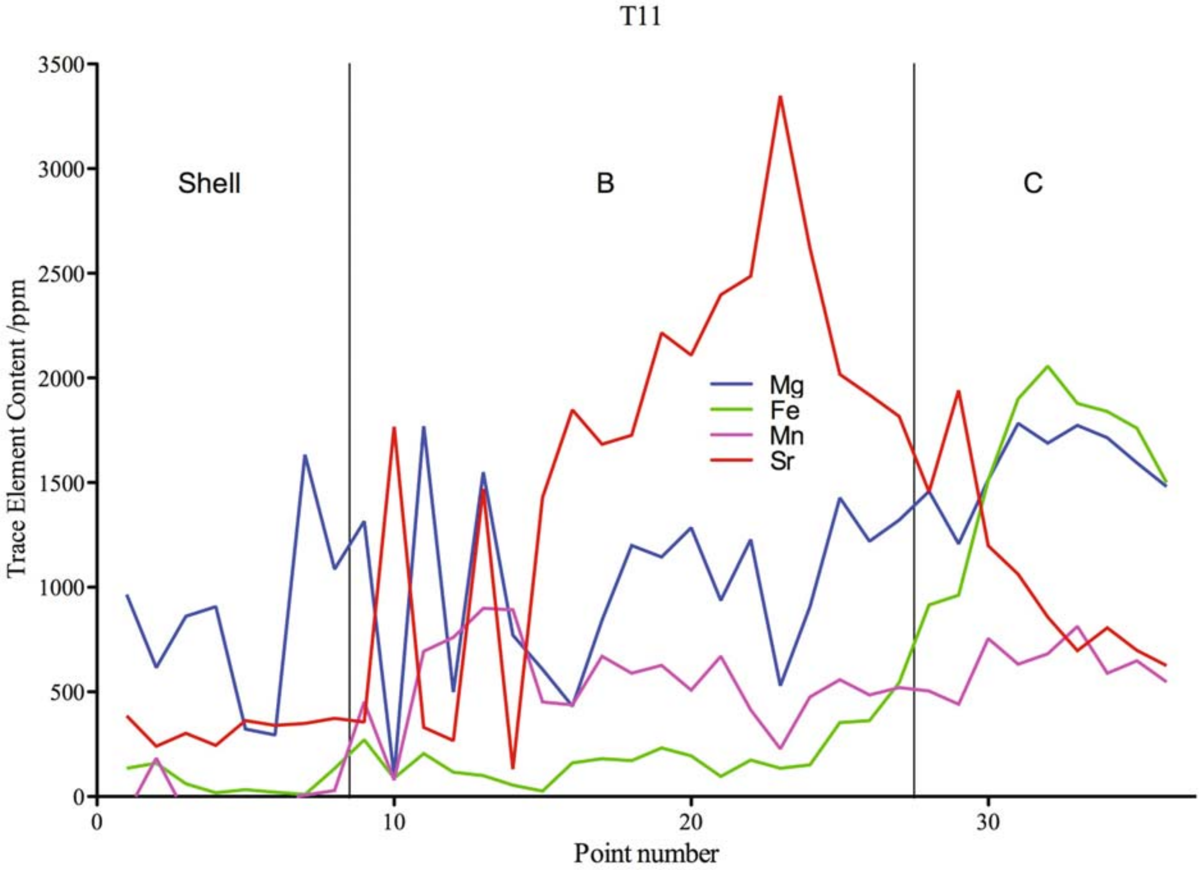
Model trace elements: The general correlation in the southern part of Lincolnshire between the preservation of the Upper Pink Band at Tetford and South Thoresby and the low values of Fe and Mn in the model cement (Text-fig. 17) suggests that the regional sulphidization and dissolution of the red pigment provided part or all of the Fe and Mn that was incorporated in the model cement during the final period of precipitation. At Tetford, South Thoresby and Welton the Sr and Mg contents of the model cement show antipathetic relations (Text-fig. 17) – a similar antipathetic relationship is present in Unit B where it is more extensive with better development, and its interpretation will be dealt with later.

A direct indication of the trace element geochemistry and the sequence of cements responsible for the hardening is provided by the description by Hu *et al.* (2012) of the calcite filling the vug within the body cavity of Terebratulid T11 from Unit A at Speeton (Text-fig 18). Three growth zones are recognised, the earliest (zone A; only observed but not analysed) is very thin and irregularly developed, consisting of minute non-luminescing crystals probably of a Mg-rich calcite that line the interior of the shell. The later zones, B and C, are characterised by a chaotic and complex pattern of trace elements that Hu *et. al.* (2012) suggest is the influence of continually changing pore fluids of different compositions. The Fe and Mn contents of the later part of Zone C are enhanced and may represent the last phase of the cement that caused the hardening of the chalk in Units A and B. We are suggesting that this is related to the local mobilisation by sulphidization of Fe and Mn occurring as fine-grained oxides responsible for the colouring of the Upper Pink Band in the chalk. Such calcite cementation under anoxic condition is associated with negative δ^{13}C values (Hu *et al.* 2012) but available stable isotope data are insufficient to establish whether this is present in brachiopod T11.

Model stable isotopes: The δ^{18}O values (-4.0‰ to -10.2‰) of the model cement are always negative and are comparable to the values (-4.7‰ to -11.6‰) reported by Hu *et al.* (2012) in the cement inside brachiopods from eastern England. These authors argued that the range of values reflected increased temperature (30 to 75ºC) during cementation within marine pore fluid with little or no influence from meteoric water. The regional north to south trend (-10‰ to -4‰) in model values may be related to decreasing average temperature of cement precipitation from 70 to 33/34ºC. The δ^{13}C values of the model cement are always positive as is typical of suboxic cementation although they display a wider range of values (up to 6.9‰) compared to those found by Hu *et al.* (2012: up to 3.6%). There is a regional north to south decrease in average δ^{13}C value that could be related to a greater contribution from anoxic cementation associated with regional facies variation. This has not been recognised in the field although there are nests of contours associated with low δ^{13}C values (down to 0.6%) at Elsham and Tetford that could be related to patches of localised anoxic cementation.



Text-fig. 17. Comparison of the variation in the model values of Fe, Mn, Mg, Sr and δ^{18}O in Unit A between Caistor and Welton showing the general regional association of higher values of Fe and Mg with low values of Mn and Sr



Text-fig. 18. Trace element concentrations arranged along the direction of crystal growth for zones B and C in terebratulid T11 from Unit A, Louth Member, Ferriby Formation, Speeton (Text-fig.13 of Hu *et al*. 2012)

The model stable isotope values are comparable in their general range to those reported by Hu *et al.* (2012) from the cement-filled cavities inside brachiopods from Speeton and Hunstanton. An indication of the changing isotopic values of the cement responsible for the hardening is provided by Terebratulid T11 from Unit A at Speeton (Hu *et al.* 2012, Table 3). Stable isotope data from zones B and C indicate that $\delta^{18}O$ values became lower as the cement grew and whereas the $\delta^{13}C$ became higher, always with positive values.

Unit B

The convoluted pattern of contours displayed by the trace element and stable isotope values (Text-figs 11B to 16B) of the model cement in Unit B show little relationship to the regional bedding as defined by the base of the Variegated Beds and the various primary marl seams. This suggests that the precipitation of cement took place from pore fluids that were circulating in the lower part of the Welton Formation, although at times the pore solutions were restricted by marl seams, particularly the Green Trace Bed. The Green Trace Bed appears to have limited the upward extension of well-defined lateral gradations in model Mg and $\delta^{18}O$ values (Text-figs 13B, 15B).

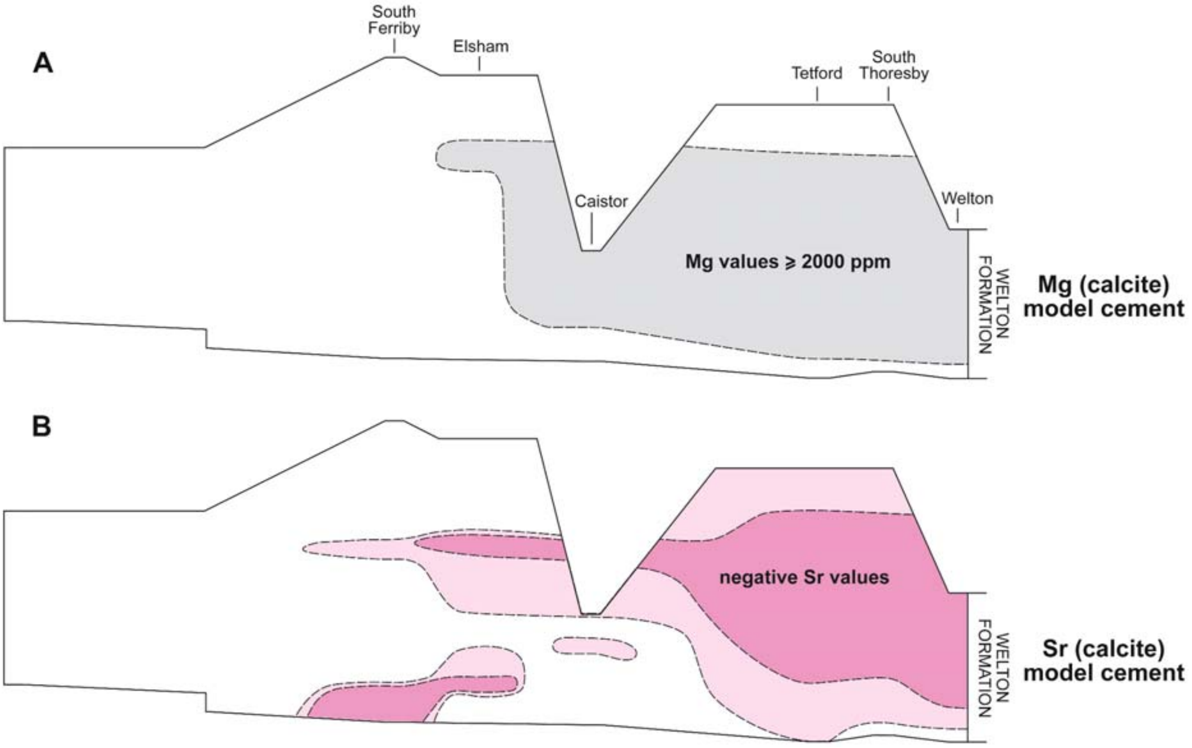
Model Trace elements: The trace element composition of the model cement in Unit B and its relationship to that of the **Standard Louth Chalk** is different from that exhibited by Unit A. Negative values are associated particularly with Sr, to a lesser extent with Mg, and occasionally with Fe and Mn.

Negative model Sr values occur in three parts of Unit B (Text-fig. 14B). The main one is extensively developed in the south and can be traced northwards to South Ferriby: the other two are more local, one includes the basal chalk at South Ferriby and is shown as confluent with the zone of negative values at Elsham between the Green Trace Bed and the base of the "chalk rich in inoceramid fragments". At Caistor there is a single sample with a negative model value. The main anomaly is best developed at Tetford where it occurs throughout the Unit in all three chalk lithofacies − the fine-grained coccolith rich chalk in the lower part, the chalk rich in inoceramid bivalve shell fragments, and in the calcisphere-rich fine grained chalk above, as well as in the flinty chalk at the top. When traced southwards to South Thoresby and Welton the base of the anomaly rises to the level of the Green Trace Bed but still within the fine-grained coccolith-rich chalk. Northwards at Elsham the anomaly is of more limited stratigraphic extent. At Elsham, and possibly at Caistor, it starts within the chalk with abundant inoceramid bivalve shell fragments and at Elsham its upper limit is within the calcisphere-rich fine-grained chalk some 75 cm below the base of the flinty chalk at the top. At South Ferriby, 10 km to the north of Elsham, this negative anomaly is represented by a single sample in the calcisphere-rich fine-grained chalk between the top of the "chalk rich in inoceramid fragments" and the base of the flinty chalk above. The stratigraphical and lateral distribution of the negative Sr anomalies demonstrates that they are not related to the original chalk lithofacies as now preserved. Much, but not all of the main negative anomaly, is developed in inoceramid-rich and calcisphere-rich chalks. Important for the interpretation of the negative model Sr anomalies is the question of whether the low Sr content of the hard chalk reflects an original compositional difference of the sediment or is the result of diagenetic processes. This can be tested with data of the chemical composition of the calcite in the bioclastic components of the soft chalk in southern England (Jeans *et al*. 1991) where it is known that the fine-grained coccolith fractions have enhanced Sr (calcite) contents compared to the coarser fractions of the Chalk. Also coccolith material (<2 μm fraction) from particular samples from the Upper Cenomanian Plenus Marls at Dover have relatively enhanced Sr (calcite) contents (~550 to 1100 ppm) but lower Mg (calcite) contents (750 to 2700 ppm) compared to the coarser particle size fractions. The same relationship, but with lower values, is seen in a chalk sample from the Coniacian or Lower Santonian of Shudy Camp in Cambridgeshire. Here the coccolith material is concentrated in the 4.47 to 0.83 μm fractions and its Sr (calcite) content, ranging from 453 to 675 ppm (average 569 ppm), is generally higher than the values from the coarser fractions. The sparse abundance of coccolith material in the coarser grained chalk rich in inoceramid remains and calcispheres may be a tempting explanation of the negative Sr values, however the calcite of inoceramid bivalves and calcispheres have relatively high Sr values that are usually in excess of the **Standard Louth Member** value (Jeans *et al.* 1991). Seventeen samples of inoceramid bivalve shell fragments and prisms from various beds in the Upper Cenomanian Plenus Marls of Dover have average Sr (calcite) values of 818 ppm Sr (range 261–1577 ppm, with two values below 550 ppm, the value for the **Standard Louth Chalk**). There is a general antipathetic correlation between the negative Sr anomalies and enhanced values of Mg in the model cement (Text-fig. 19). Considering (1) the abundance of inoceramid bivalve shell fragments and prisms and their expected high values of Mg in their calcite, judging from the 17 samples from Dover mentioned above which average 6075 ppm (range 3569–9133 ppm) and (2) the somewhat lower values for Mg for the calcisphere-enriched fractions from the same locality (2300−3200 ppm) and Shudy Camp (1829 and 1865 ppm), it might be expected that the actual Mg values associated with these lithofacies would be higher than their typical values of 1500–1900 ppm (Table 4). This suggests that both Sr and Mg may have been preferentially lost during diagenesis in a linked process. Comparison of the inoceramid bivalve shell fragments and prisms from the Plenus Marls of Dover (Jeans *et al.* 1991, fig. 4d), assumed to be unaltered or very little altered, with those in Text-fig. 9C from Elsham shows a general difference. The calcite of those from Dover is full of inclusions, whereas those from Elsham range from being clear crystals to containing some inclusions suggesting complete or partial recrystallization. There is also petrographic evidence that recrystallization may have also affected calcispheres and shell fragments. We suggest that the original biogenic calcite on recrystallization excluded or greatly reduced the amount of Sr (ionic radius 1.27Å) and Mg (ionic radius 0.78Å) in the recrystallized calcite because of their mismatch with Ca (ionic radius 1.06Å) within the calcite lattice. Our interpretation of this negative Sr anomaly as a post-depositional effect, essentially unrelated to the original lithofacies, is given further support because a low Sr but still positive anomaly occurs also in the underlying Unit A between Caistor and Welton (Text-fig. 17) but in a different chalk lithofacies.

Another contributing factor to the development of the negative Sr anomalies must have been the dissolution of aragonite shells during early diagenesis. Aragonite with its appreciable contents of Sr, when compared to calcite, is an important source of this trace element in early calcite cements in the Chalk (Hu *et al*. 2012, text-fig. 27). In those parts of the chalk reservoir that were tight the Sr would have been retained in the pore fluids, to be incorporated either into carbonate cements or other Sr-containing authigenic minerals. If, however the reservoir was leaking during early diagenesis as we have suggested for Units A and B in southern Lincolnshire, the Sr-enriched pore fluids would be lost. Although aragonite is not preserved in either Units A or B there can be no doubt that it was present as the calcitic portions of inoceramid bivalves are preserved. These bivalves originally consisted of both calcite and aragonite and only the individual calcite prisms or fragments of shell consisting of these prisms are preserved. In Unit A they are a minor or occasional component but in Unit B these prisms and shell fragments are particularly abundant in the chalk above the Green Trace Bed (Text-fig. 5). In addition to inoceramid bivalves, there were likely to have been the remains of many other invertebrates with skeletons consisting solely or partially of aragonite, such as ammonites, gastropods and bivalves.

Negative model Mg values at Flixton are restricted to the chalk between the top of the Variegated Beds and the Green Trace Bed (Text-fig. 13B). The lithofacies is a fine-grained coccolith-rich chalk with scattered planktonic foraminifera and calcispheres. When this subunit is traced southwards the negative Mg values are gradually replaced by positive values. Beyond Elsham, values are all positive and increase generally southwards. This pattern is parallel to those exhibited by the $\delta^{18}O$ values of the model cement and to thickness variations of the Variegated Beds. The most negative Mg values are associated with the lowest $\delta^{18}O$ values and the thickest section of the underlying Variegated Beds. A possible clue to this relationship may be the direct correlation between the volume of the clay mineral assemblage and bed thickness – the greater the thickness the greater the amount of the clay assemblage. The Variegated Beds are dominated by the Chalk smectite-mica clay assemblage (Jeans 1968; Wood *et al*. 1997). The smectite component is considered by Weir and Catt (1965) to be a dioctahedral smectite containing Mg as an interlayer cation as well as occupying sites in the octahedral layer. There is considerable discussion about the origin of the smectite (Hu *et al*. 2014); is it detrital or has it been neoformed within the chalk sediment during diagenesis, possibly as the result of the argillization of volcanic ash? A possible explanation of the lateral pattern of Mg in the model cement of this lowest subunit of Unit B is that the neoformation of the Mg-containing Chalk smectite in the Variegated Beds depleted not only its own porewaters in Mg but also that of the overlying chalk subunit; the extent of this depletion being controlled by the amount of smectite being formed and this is reflected in the thickness of the beds.

Negative model Fe values are restricted to a single sample at Tetford and to four zones at Flixton (Text-fig. 11B). At Tetford it is associated with the highest $\delta^{18}O$ value of the model cement in Unit B, whereas those at



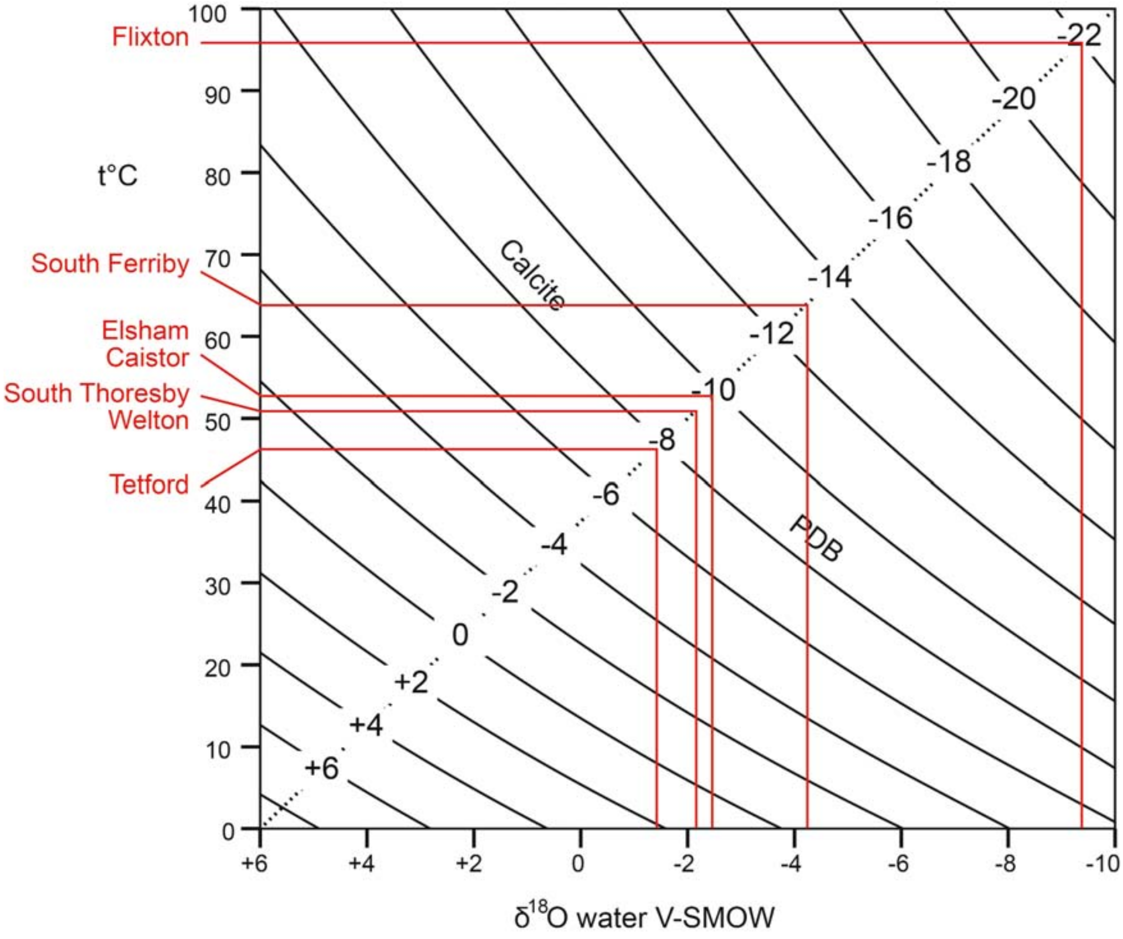
Text-fig. 19. Unit B in Lincolnshire showing the antipathetic relationship in the model cement between Mg values of 2000 ppm and above and negative values of Sr. (key as for Text-fig. 14)

Flixton are not associated with relatively high $\delta^{18}O$ values. At both locations a possible cause is the localised depletion of the Chalk's pore waters by the development of authigenic clay assemblages enriched in Fe. At Tetford the high $\delta^{18}O$ value suggests that here it is more likely to be associated with early cementation.

A single negative model Mn value is associated with the Green Trace Bed at Elsham (Text-fig. 12B). A possible cause is the localised depletion in Mn of the pore fluid of the chalk as the result of the formation of a Mn-enriched diagenetic mineral .

Model stable isotopes: The $\delta^{18}O$ values display two conspicuous patterns. The first is associated with the chalk between the top of the Variegated Beds and the Green Trace Bed in Unit B. At Flixton it has exceptionally isotopically light values as low as $\delta^{18}O$ of -22‰. As this chalk subunit is followed southwards values become increasingly high, reaching -9 to -8‰ in south Lincolnshire. There is independent evidence of a maximum temperature of ~110ºC based on spore colouration index values (averaging 4) affecting the immediately underlying Variegated Beds at Flixton (Cornford in Jeans *et al*. 1991; Cornford 1998, fig. 11.17.(3)). If this represents the average temperature (~95ºC) of calcite cement precipitation in the immediately overlying chalk at Flixton, the model cement $\delta^{18}O$ value of -22‰ could have been precipitated in equilibrium with a marine pore fluid with a water $\delta^{18}O$ of 9 to 9.5‰ V-SMOW (Text-fig. 20). The regional increase in $\delta^{18}O$ values of the model cement represents a decrease to about 50ºC in south Lincolnshire. Depth of burial curves (Hu *et al.* 2012, text-figs 24, 25) based upon the cement within brachiopods do not suggest enhanced burial in the north. However the enhanced temperature and its regional pattern could have resulted from the injection of hot mineralising fluid which precipitated a calcite cement into this chalk subunit between the Green Trace Bed and the top of the underlying Variegated Beds in the north, and which cooled as it travelled southwards.

The second conspicuous pattern is a region of high $\delta^{18}O$ values centred at Elsham that cuts across the



Text-fig. 20. Cross plot of temperature and $\delta^{18}O$ for the equilibrium precipitation of calcite in sea water showing the temperatures of precipitation of the model cement in the basal chalk subunit of Unit B at various locations in eastern England stratigraphy of Unit B. It is recognised at South Ferriby and extends southwards as a finger of isotopically heavy values that is evident at Caistor and Tetford. There is some correlation between this region of high $\delta^{18}O$ values and a whale-shaped zone of high Fe contents (1000–2000 ppm) in the model cement (Text-fig. 11B). This could represent a phase of enhanced Fe-rich cement associated with cooler pore water.

The zone of low $\delta^{18}O$ values and the region of high $\delta^{18}O$ values intersect in the lower part of the section at Elsham. The contours suggest that the zone of high $\delta^{18}O$ (lower temperature) cement was already in place when the zone of lower $\delta^{18}O$ (higher temperature) cement was precipitated in the chalk sub-unit between the top of the Variegated Beds and the Green Trace Bed.

GENERAL INTERPRETATION

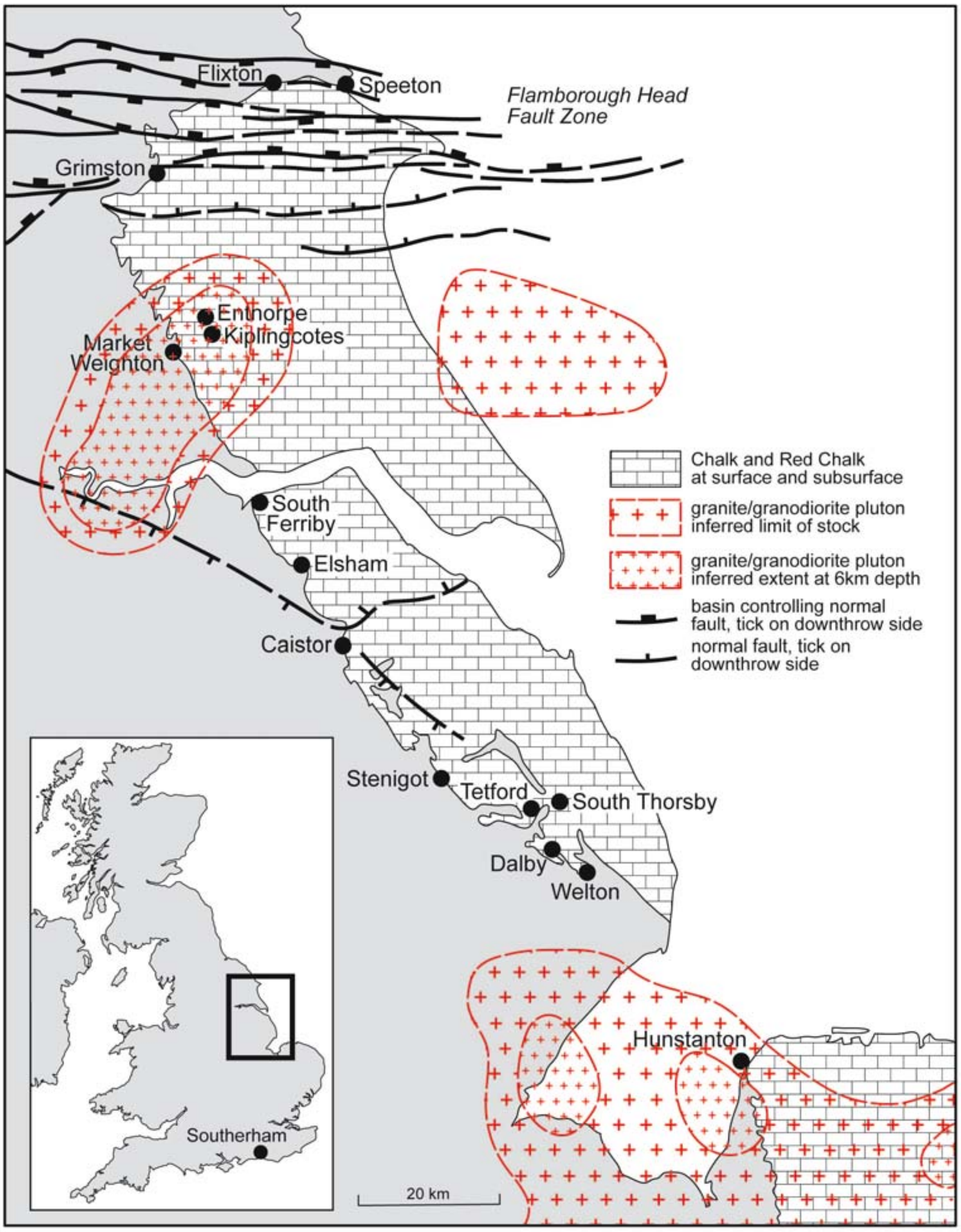
The different and convoluted concentration patterns of trace elements and stable isotope values in the model cements of Units A and B indicate that their precipitation took place in two separate chalk cells separated by the thin but clay-rich Variegated Beds acting as an effective seal. In Unit A, the concentration patterns show practically no correlation with the general direction of bedding, reflecting the homogeneous nature of its primary lithofacies and the lack of primary marl bands. In Unit B, with its more varied lithology and the presence of laterally continuous primary marl bands, there is more correlation. The subunit of fine-grained chalk between the base of the Unit and the Green Trace Bed displays strong north-south regional patterns in the Mg and $\delta^{18}O$ values (Text-figs 13B, 15B). In Lincolnshire, high values of Mg and negative values of Sr are associated with but not restricted to the lithofacies rich in inoceramid bivalve shell fragments and calcispheres (Text-figs 13B, 14B). The regional values for Mn display a general up-sequence decrease in values (Text-fig. 12). In spite of these differences the overall diagenetic history of units A and B is similar. Each underwent a main period of cementation under conditions of considerable overpressure, maintaining an abnormally high porosity and permeability, thus allowing the relatively free circulation of the pore fluids from which calcite cements were precipitated. The average $\delta^{13}C$ values of the cement were positive and precipitation took place on average under suboxic conditions (suboxic type of Hu *et al.* 2012). The overall style of cementation is in contrast to that which characterizes the lower and main part of the Ferriby Formation with its localised centres of cementation and diagenetically earlier lithification. However the trace element pattern in the cement in Terebratulid T11 from Unit A at Speeton (Text-fig. 18) is comparable to that of other brachiopods (T5, T7–10) from the lower part of the Ferriby Formation at Speeton investigated by Hu *et al.* (2012) that were involved in early lithification prior to the loss of overpressure, and these also display similar chaotic trace element patterns.

The absence of conspicuous evidence of early lithification in Units A and B reflects their more off-shore depositional sites and differences in the bioclastic composition of the sediment entering the diagenetic environment. For example, the chalk of Unit A is a distal facies representing relatively rapid deposition with a very restricted benthic fossil assemblage. The rarity of fossils with shells consisting wholly or partially of aragonite suggests this early and important source of $CaCO_3$ for cement was limiting. Cement precipitation did take place: it occurred generally throughout the sediment but was insufficient to form lithified compaction-resistant structures that would be emphasised by subaerial weathering. Such lithified structures would be capable of brittle fracture during the overpressure phase of diagenesis as evident in the Breccia-Nodule Bed in the Red Chalk Formation at Speeton (Jeans 1973, p. 429).

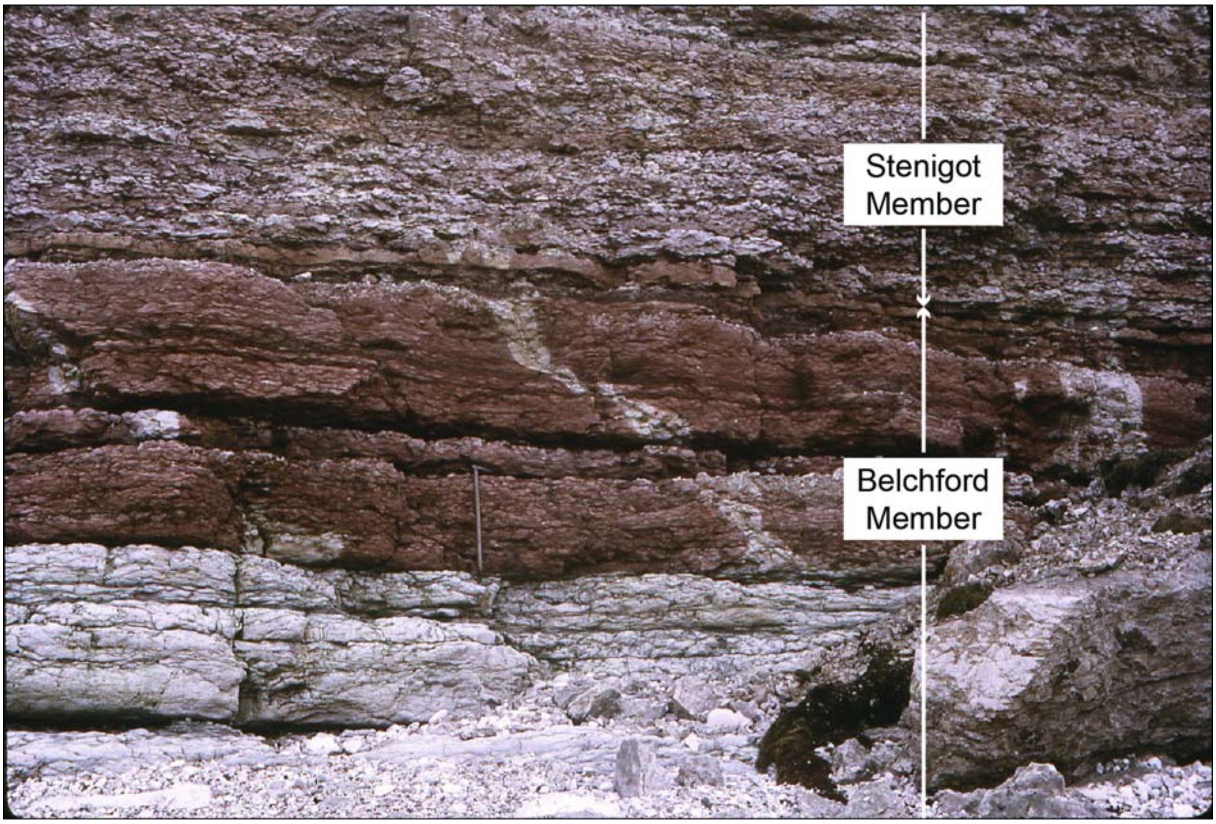
The phase of overpressured diagenesis in eastern England was brought to an end at the same time in both units by regional tectonic activity which allowed the overpressured pore fluids to escape either to regions of lower pressure or to the surface. At least partially responsible for this was the reactivation of a number of basement structures that are deduced to, or can be seen to, affect the Chalk (Text-figs 3, 21). The most prominent is the Flamborough Fault Zone (the reactivation of the Jurassic Howardian Fault Belt; Text-fig. 21) that is responsible for the E–W Contortion Zone in the Chalk with its complex folding, faulting and jointing which is exposed in the cliffs at Flamborough. The WSW–ENE Caistor Fault is responsible for localised folding in north Lincolnshire. Associated with the Wash and north Norfolk is a postulated WNW–ESE tectonic line (the Wash Line of Jeans 1980) that affected the Chalk of south Lincolnshire which may represent the northern margin of the buried granite mass in the basement underlying Norfolk (Text-fig. 21: Pharaoh *et al.* 1996). There is evidence that the initial reactivation of these three basement structures was already under way during the overpressured phase of diagenesis. Activity on the Flamborough Fault Zone may be responsible for the introduction of the postulated hot, calcite-precipitating solution into the basal subunit of Unit B that affected this horizon as far as south Lincolnshire. Less certain is the possible association between the complex zone of $\delta^{18}O$ contours in Unit B at Elsham and the

Caistor Fault somewhat further to the south or to its extension to the north-west. The loss of pore solutions rich in Sr and Mg in southern Lincolnshire during early diagenesis in both Units A and B is probably related to pore pressure leakage along the WNW–ESE 'Wash Line' to the south.

The next phase in the diagenesis of Units A and B is intimately related to the increase in grain pressure associated with the loss of overpressure in the pore fluids and the influence of the three reactivated basement structures. This was associated regionally with grain welding, pressure dissolution of the calcite grains and the general precipitation of a calcite cement. It resulted in lithification and the associated development of brittle fracture, pressure dissolution marl seams, stylolites, and wisps. Figure 6b in Jeans (1980) illustrates the intimate relationship between pressure dissolution and the development of stylolites, marl seams, and brittle fracture in the Louth Member (Unit A) of the Ferriby Formation at South Thoresby. Directly linked to the Flamborough Fault Zone and the Caistor Fault, and less certainly to the WNW–ESE 'Wash Line', are zones of



Text-fig. 21. Regional map of eastern England and the adjacent parts of the North Sea showing the distribution of the Chalk at the surface and subsurface, the main tectonic structural lines and the granites inferred to occur at depth. Based on Pharaoh *et al.* (1996)



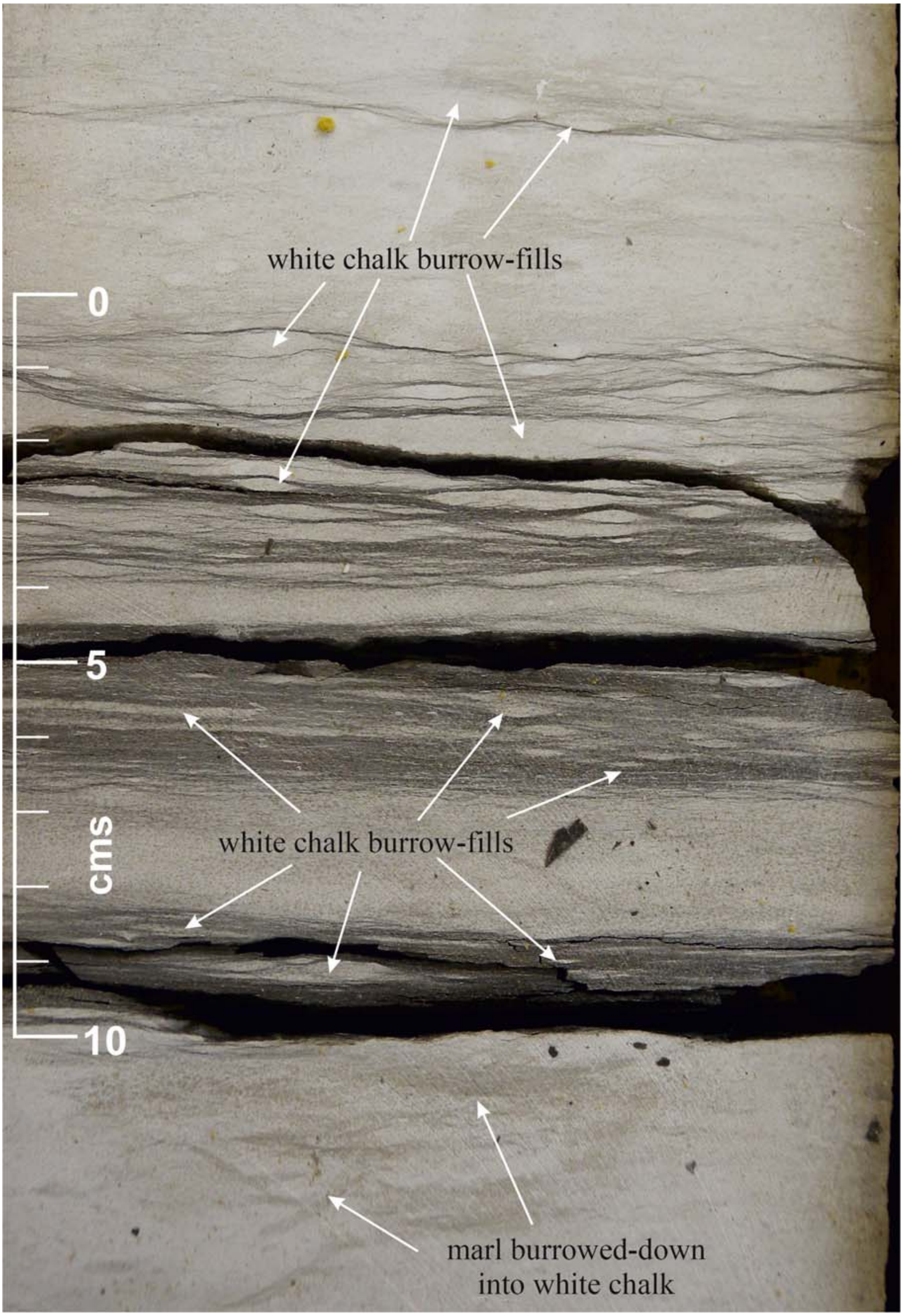
Text-fig. 22. The Ferriby Formation at Red Cliff, Speeton showing the Belchford Member overlain by the Stenigot Member. The lower part of the Belchford is bluish-greyish white as a result of sulphidization and contains pyrite and marcasite crystals. Three narrow zones of sulphidization extend upwards on either side of inclined fractures that cross-cut the reddish brown coloured chalk of the upper part of the Belchford Member. These disappear into the marbled pink and white nodular chalk of the overlying Stenigot Member. Scale, ice axe, 86 cm

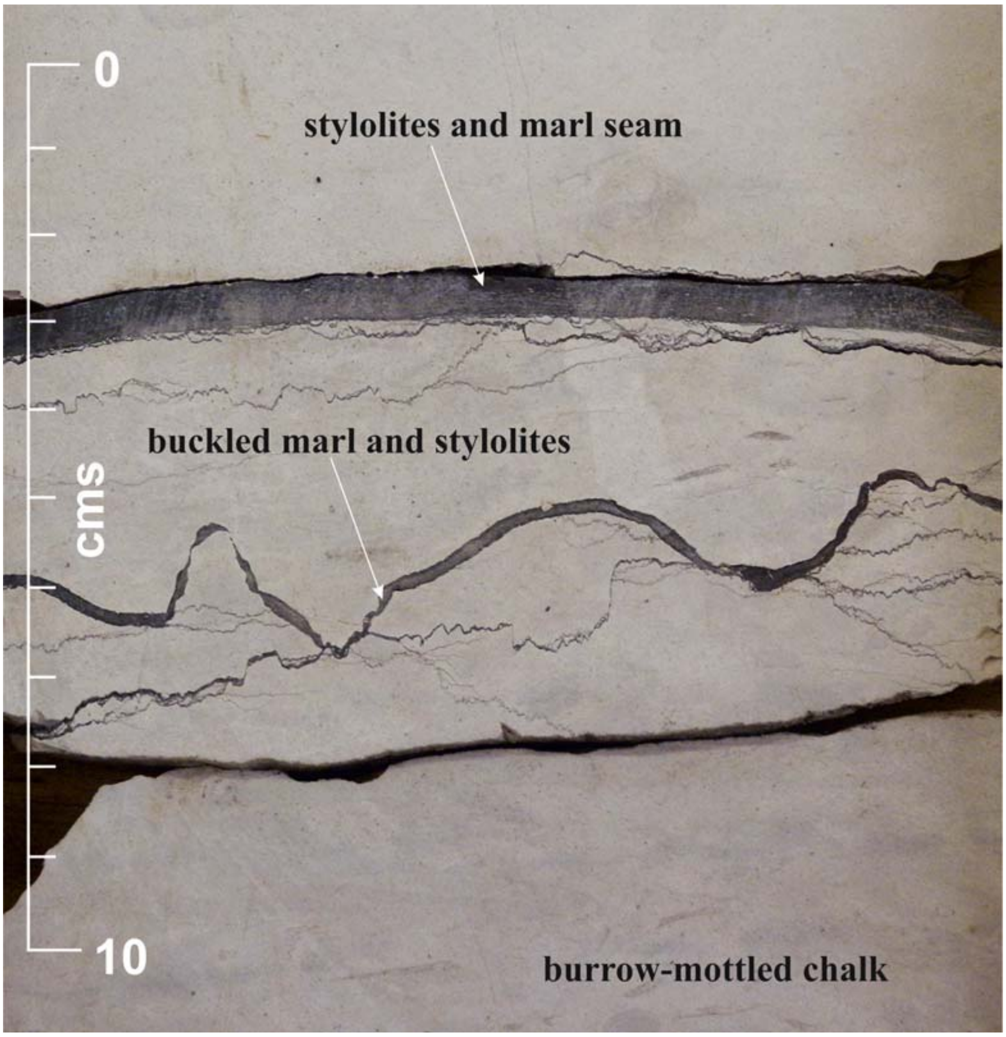
sulphidization that cut across the stratigraphy of the Red Chalk and Ferriby formations (Text-fig. 3). These are responsible for the loss of the Lower and Upper Pink Bands over much of Lincolnshire and Yorkshire as well as the red colour of the Red Chalk Formation at Caistor, Grimston and locally at Speeton (Text-fig. 3). Unpublished sulphur isotope studies on the pyrite nodules and the chalk from these discoloured chalks leave little doubt that this alteration was under the control of sulphate-reducing bacteria acting on allochthonous pore fluids rich in sulphate and hydrocarbons (Jeans, Turchyn, Hu and Mortimore in preparation). It is postulated that the solutions, ascending along these fault lines, were forced out of the North Sea Basin by increased lithostatic pressure possibly during a single or a number of tensional phases of tectonic activity. The timing of this is not clear. Starmer (1995, 2008, 2013) has identified four tectonic phases (D1−D4) in the Chalk affected by the Flamborough Fault Zone. D1 (Laramide – late Maastrichtian to early Palaeocene) and D3 (Alpine – Oligocene) were compressional and involved in folding and thrusting, whereas D2 (post-Laramide – late Palaeocene and Eocene) and D4 (post-Alpine – Miocene to Pliocene) are tensional phases involved with normal faulting and jointing. Obviously a tensional regime is a more likely scenario for these ascending sulphate- and hydrocarbon-rich fluids, but at present there is no field evidence to make a specific case for one phase or the other. It is clear at Speeton that these solutions made use of joints to ascend the succession, diffusing out laterally into the more permeable beds (Text-fig. 22). Some of this movement could have been earlier during the Late Cretaceous but cannot be demonstrated onshore because of the loss of the Campanian–Maastrichtian and Tertiary sediments. Offshore, along the Dowsing–South Hewett Fault Zone, which links in to the Flamborough Fault Belt, there is evidence from seismic sections for Santonian−Campanian and Maastrichtian tectonic events leading to local unconformities on tectonic structures (fault-driven uplift: Badley *et al.*1989). It is quite possible that the ending of the first phase of overpressured diagenesis could have been pulsed, varying in its timing and regional effects over eastern England.

Text-fig. 23. Encrustation of large calcite crystals from an open joint in the Chalk of Selwick Bay, Yorkshire. Scale in cm

The second phase of cementation in Units A and B is not just a simple redistribution and re-precipitation of the chalk and its earlier cement (dissolved by pressure dissolution) to form the hard chalk as we know it today. The calcite dissolved was not reprecipitated in the immediate environment as would be expected with pressure solution (Jeans 1980, pp. 94–97). It was released into an open system affected by the developing pattern of brittle fractures as lithification occurred. Some of the $CaCO_3$ migrated elsewhere to be precipitated as vein and vug filling calcite (Text-fig. 23), whereas some was precipitated in the surrounding chalk incorporating enhanced amounts of Fe and Mn that had been mobilised locally by the microbial reduction of the fine-grained red and ochreous pigments responsible for the coloured horizons in the Red Chalk and Ferriby formations. This is reflected by the particular low values of Fe and Mn in the model cement of Unit A at Tetford and South Thoresby in south Lincolnshire where its pink colour (Upper Pink Band) is preserved. There is little direct evidence of the geochemistry of this second phase of cement. In those parts of Units A and B affected by sulphidization the cement is likely to be enriched in Fe and Mn; it would also be expected to have negative $\delta^{13}C$ values as evidence suggests it developed under anoxic conditions through the action of sulphate-reducing bacteria (cf. anoxic cement series of Hu *et al.* 2012). The final stages of the cement sequence recorded in Zone C from Terebratulid T11 (Text-fig. 18) collected from the sulphidized Unit A at Speeton does display an enrichment in Fe and Mn but the analysis of the bulk calcite from this zone gives a positive $\delta^{13}C$ value of 3.52 ‰ that does not indicate precipitation under anoxic conditions. It is possible that more detailed analysis of Zone C with higher spatial resolution using laser ablation or ionmicroprobe isotope analysis might reveal that the final Fe and Mn enrichment in the cement took place under anoxic conditions.

Driving the circulation of pore fluids in Units A and B must have been effected by variations in compaction, pore fluid pressure, tectonic activity and temperature.


white chalk burrow-fills
0
5
cms
10
white chalk burrow-fills
marl burrowed-down into white chalk



Text-fig. 25. High density white chalk (SG >1.95) from the North Sea showing primary marl seams that have been secondarily compressed and buckled in association with the development of syn-deformational stylolites and secondary marl seams. (from Mortimore, 2014, figure 5.37)

The pattern of $\delta^{18}O$ values of the model cement provides indication of the variation in temperature as long as it is accepted that calcite precipitation took place in marine pore waters as is evident from the calcite cement preserved in Terebratulid T11 from Unit A and other brachiopods from stratigraphically lower levels in the Ferriby Formation at Speeton (Hu *et al.* 2012) – although there is no direct evidence for Unit B. In both units enhanced temperatures are recorded in the northern part of the region. Unit A has a regional decrease in temperature from an average of 70ºC in the north to 33–34ºC in the south. Unit B displays two patterns. Initially a cooler and variable pattern of temperature (35 to 50ºC) was established with a zone of greatest variability centred on Elsham. Later, but still during the first and overpressured phase of cementation, hot calcite-precipitating solutions were injected between the base of Unit B and the Green Trace Bed; at Flixton the temperature of cement precipitation was ~95ºC and the effects of this can be recognised in the same subunit in south Lincolnshire where the temperature had dropped to ~50ºC. There is no clear relationship to the granites (Pharaoh *et al*. 1996) postulated to underlie the Market Weighton Block and north Norfolk (Text-fig. 21), and these lateral changes are best related to variations in heat flow and hydrothermal activity associated with various phases of tectonic activity in the North Sea Basin.

Text-fig. 24. High density white chalk (SG >1.95) from the North Sea displaying a complex primary sedimentary marl seam with an extensive burrow networks with white-chalk burrow-fills that have been squashed and sheared in the lower parts of the bed as a result of post sedimentary compaction and bedding-slip (from Mortimore 2014 figure 5.29)

CONCLUDING DISCUSSION

A novel approach has been applied to investigating the regional hardening of the Chalk of eastern England by modelling the extent and geochemistry of its cement based upon the **Standard Louth Chalk**. The interpretation of the patterns of variations shown by the major trace elements and the $\delta^{18}O$ and $\delta^{13}C$ values has revealed details of a surprisingly complicated history, very different from the simple idea that pressure solution or pressure dissolution and reprecipitation, with or without the introduction of meteoric water, were the causes of the change from soft to regionally hardened chalk as a result of burial and temperature increases (Wolfe 1968; Scholle 1974; Neugebauer 1973, 1974; Maliva and Dickson 1997) or tectonic activity (Mimram 1975, 1977, 1978).

We suggest that overpressuring, with the Variegated Beds acting as a seal between these adjacent units, played an important role in allowing pore fluids to circulate independently of each other on a regional and local scale. It has already been suggested that the Variegated Beds, rich in smectitic clay, was responsible for the trapping of compaction-driven pore waters and the development of overpressure in the top part (Unit A) of the Ferriby Formation (Hu *et al.* 2012, text-fig. 26). Responsible for the development or enhancement of overpressures in Unit B would have been the restrictions on the upward movement of compaction-driven pore waters by the fine-grained chalk of low permeability and the numerous thin and laterally extensive primary marl bands and flint horizons in the overlying Chalk described by Wood and Smith (1978) and Whitham (1991).

Evidence suggests that our conclusions based upon the two units (A, B) may not apply to the main mass of hard white chalk that overlies them. Units A and B represent sedimentation at the end of a period of deposition (Cenomanian to Mid Turonian) in which early lithification – nodular chalks and hardgrounds – and shallow water facies are widespread. In contrast the overlying Chalk (Mid Turonian to Campanian) displays little or no evidence of early lithification or shallow water facies.

Modelling of the geochemistry of the cement in Units A and B and the geochemistry of the calcite crystals developed within the body cavities of brachiopods (Hu *et al*. 2012) from the underlying chalk of Cenomanian age indicates that cementation is microbially influenced and the source of the calcite cement lies with the aragonite shell material present in the sediment. So the absence of early lithification in the younger chalks does not reflect the absence of the different microbial groups that played a role in calcite precipitation, but the lack or shortage of aragonite shell material in the more off-shore and deeper water chalk sediment. Studies on the main mass of hard chalk in eastern England are restricted to Scholle's (1974) and Mimram's (1978) investigations of the Chalk around Flamborough in Yorkshire. Their contrasted observations on the extent of sediment compaction and the crushing of microfossils suggest that they sampled chalks of rather different diagenetic histories. Scholle's samples exhibited considerable compaction but he states that it is less extensive than that he observed in the Irish Chalk where Wolfe (1968) had measured 15−31% compaction based on fossil crushing. In contrast, Mimran's samples showed no evidence of compaction. In addition to these differences in compaction, there are differences in porosity. The uncompacted samples have porosities between 17 and 8 vol. % (Mimram 1978), which suggest bulk specific gravities between 2.24 and 2.48, whereas the compacted chalks have higher porosities (17−20 vol. %; Scholle 1974) with bulk specific gravities of 2.16 to 2.24. This suggests that the uncrushed chalks have undergone lithification by calcite cementation prior to potential fossil crushing, whereas the crushed chalks experienced compaction prior to lithification and cementation. The general absence of early lithification in the Mid Turonian to Campanian Chalk of eastern England suggests that originally this was soft and uncemented similar to the soft chalks of south-east England. Supporting evidence of this includes: (1) the Yorkshire Chalk in the area of Enthorpe and Kiplingcotes is soft and unhardened with bulk specific gravities (based on 5 samples from the Enthorpe railway cutting) ranging from 1.58 to 1.66, averaging 1.64, no different from the average value for the uncemented **Standard Louth Chalk** at Dover, and (2) soft and uncemented chalks are known in boreholes put down to investigate the foundations for off-shore wind farms only 10−15 km off Flamborough Head (Mortimore and James 2014). A likely explanation of the local soft Yorkshire Chalk is that it was originally highly overpressured − as suggested for the chalk of Units A and B – but the grain pressure was sufficiently low that pressure dissolution of the calcite grains did not take place. Subsequent loss of overpressure and the associated enhancement of grain pressure may have taken place at a shallow burial depth, considerably less than the 1000 m which Neugebauer (1973, 1974) has calculated as the minimum depth of burial for a low-Mg calcite sediment − such as the chalk − to be affected slightly by pressure solution and cementation (0.5−5%).

The spatial arrangement, shape and dimensions of the bodies of compacted and uncompacted chalks reported by Scholle (1974) and Mimram (1978) is unknown, they could parallel the general direction of bedding or be independent of it, perhaps associated with cross-cutting structures. A hypothetical scenario envisages two adjacent bodies of overpressured, unlithified and uncemented chalk. In one body there is a gradual and localised leakage of pore fluids. Developing in the immediate environment of the leakage are enhanced grain pressures, fossil compaction and pressure dissolution of the calcite grains. Part of these pore solutions, enriched in calcium carbonate, is lost to lower pressure regions outside the chalk body, whereas some migrates in the opposite direction along a gradient in pore fluid pressure related to a minor loss of pore pressure in the adjacent chalk body. Along this more extended pathway there is sufficient time for the calcium carbonate to be precipitated out as calcite cement. Such a situation could develop in overpressured, uncemented chalks that were being affected by tectonic movement. It is clear that a careful investigation of the distribution of compacted and uncompacted chalks in the Mid Turonian to Campanian chalks of east England and their relationship to the tectonic framework as well as the postulated granitic intrusion underlying the Market Weighton Block (Text-fig. 21) is needed before their geological history can be resolved.

Considerable progress in understanding the regional and geological significance of the variations in the Chalk's hardness is likely to come from studies in the North Sea. The surveying of certain sites for off-shore wind farms has demonstrated that where the Chalk is cut by faults on structural highs it is much harder and more dense than the soft chalks of the equivalent horizons in the off-structural regions (Mortimore and James 2014). Features developed in these hard chalks are the result of the deformation of primary marl seams and burrow textures by compaction and bedding slip (Text-fig. 24) and the development of stylolites, secondary marl seams and brittle fracture by pressure dissolution and calcite cementation (Text-fig. 25). This overall setting is similar to that we have described onshore in Units A and B, where it has been interpreted as the effects of the great increase in grain pressure when the seal on an overpressured reservoir fails. However, pending a detailed investigation of the hardening, the presence or absence of a microbially influenced phase of calcite cementation cannot be assumed.

The approach we have taken by comparing the geochemistry of equivalent hard and soft chalks and then attempting to differentiate by modelling whether (1) an additional cement has been added, or (2) the cement is no more than the pressure solution effects on the original sediment in a closed system, or (3) the hardening is not related to cementation but to the complex interlocking of the original calcitic bioclastic grains affected by pressure dissolution in an open system where the dissolved $CaCO_3$ is lost. When this is combined with the analysis of the large calcite cement crystals that may have grown inside fossil echinoid tests or within brachiopods or bivalves, it will open up a new chapter in the understanding of the regional hardening of the Chalk as well as other limestones that are generally too fine-grained for satisfactory microscopic investigation of their diagenesis and geochemistry.

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