

# Calcite cements and the stratigraphical significance of the marine $\delta^{13}\text{C}$ carbonate reference curve for the Upper Cretaceous Chalk of England

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## ABSTRACT:

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The hypothesis of Jarvis *et al.* (2006) that a  $\delta^{13}\text{C}$  (calcite) reference curve based upon bulk samples from the Upper Cretaceous Chalk of England can be used as a primary criterion for trans-continental correlation is reviewed in the light of new stable isotope data from the Upper Albian and Cenomanian chalks of eastern England and from the Cenomanian to Campanian chalks of southern England. Evidence demonstrates that in the coloured chalks of eastern England the cements invariably have positive  $\delta^{13}\text{C}$  values (up to 3.5‰) except where they have been affected by hardground development when the cements have negative  $\delta^{13}\text{C}$  values down to –6.5‰. In contrast, the White Chalk of southern England may have cements with  $\delta^{13}\text{C}$  values as negative as –8‰. Modelling indicates that the coloured chalks may preserve a truer record of the primary palaeo-oceanographic  $\delta^{13}\text{C}$  signal than the white and grey chalks of southern England. It is suggested that (1) many of the 72 isotope events described from the  $\delta^{13}\text{C}$  (calcite) reference curve and proposed for correlation may reflect the effects of variations in the type and extent of calcite cementation; and (2) until much more is known about the patterns of calcite cementation in the Upper Cretaceous Chalk the use of minor isotope events for trans-continental stratigraphic correlation can only be applied with the utmost caution.

**Keywords:** Cretaceous; Correlation;  $\delta^{13}\text{C}$  reference curve; Isotope events; Calcite cement; Chemostratigraphy; Limitations.

## INTRODUCTION

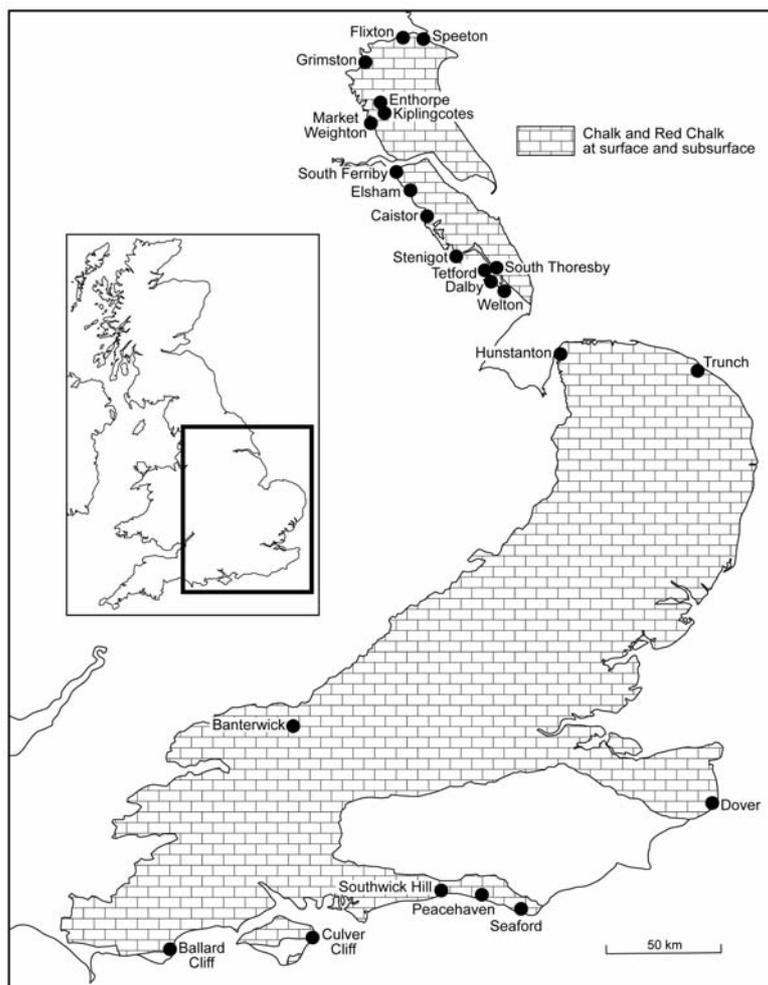
Scholle and Arthur (1980) were the first to explore the possibility that variations of the  $\delta^{13}\text{C}$  (calcite) values from pelagic limestones were a potential tool for long-range correlation in the Cretaceous sediments of circum-Atlantic-Western Tethyan region including Chalk sequences in the UK (Kent, Hampshire, Norfolk), North Sea, Netherlands and Germany. These authors were at

pains to discuss possible problems relating to primary controls on the carbon isotope variations related to temperature, water mass and faunal/floral changes, the organic carbon cycle as well as to diagenesis. They drew the conclusion that there are major fluctuations in carbon isotope values that can be correlated over distances of thousands of kilometres and these may be associated with palaeo-oceanographic or palaeocirculation events. Four important  $\delta^{13}\text{C}$  episodes were recognised: A heavy event

close to the Cenomanian–Turonian boundary, light events close to the Albian–Cenomanian, Turonian–Coniacian and Maastrichtian–Danian boundaries. This initial foray into using the pattern of  $\delta^{13}\text{C}$  values in the Chalk for stratigraphical purposes was followed up by more detailed and extensive sampling at  $\sim 1$  metre intervals of the English Chalk and its comparison to the Italian Scaglia (Jenkyns *et al.* 1994). There were also detailed investigations of the  $\delta^{13}\text{C}$  patterns in parts of the Cenomanian and Lower Turonian Chalk related to a possible Mid Cenomanian Event (Paul *et al.* 1994) and the Cenomanian–Turonian Anoxic Event (Jarvis *et al.* 1988; Leary and Peryt 1991; Gale *et al.* 1993; Mitchell 1995, 1996; Mitchell *et al.* 1996; Paul *et al.* 1999; Jarvis *et al.* 2001; Keller *et al.* 2001; Tsikos *et al.* 2004). More recently a composite  $\delta^{13}\text{C}$  carbonate reference curve based upon 1769 bulk samples for the Cenomanian–Campanian Chalk sequence of England has been established and 72 isotope events have been defined in relation to 45 biostratigraphical markers (Jarvis *et al.* 2006). It is suggested that these isotope events are

isochronous and the resulting chemostratigraphy can be used as a primary criterion in trans-continental correlation.

The purpose of this paper is to demonstrate that too little regard has been given to the effects of calcite cementation modifying the primary  $\delta^{13}\text{C}$  value of the sediment thus ignoring the possibility that much of the  $\delta^{13}\text{C}$  reference curve (Jarvis *et al.* 2006) may be unsuitable for detailed stratigraphical correlation. The first part summarises new information (unavailable to earlier authors) on the geochemistry of the calcite cements associated with the Chalk which display  $\delta^{13}\text{C}$  values ranging from 3.5‰ to –8‰. The second uses these new geochemical data to show the effects on bulk chalk samples of introducing varying volumes of cement of known isotopic composition. The third part considers evidence for diagenetic effects on the  $\delta^{13}\text{C}$  (calcite) values in the English Chalk making use of the patterns of  $\delta^{18}\text{O}$  carbonate values, trace element concentrations in the calcite and the amount of acid insoluble residue. The last part discusses the significance of our findings in



Text-fig. 1. Distribution of the Chalk and Red Chalk in the UK showing locations mentioned in the text

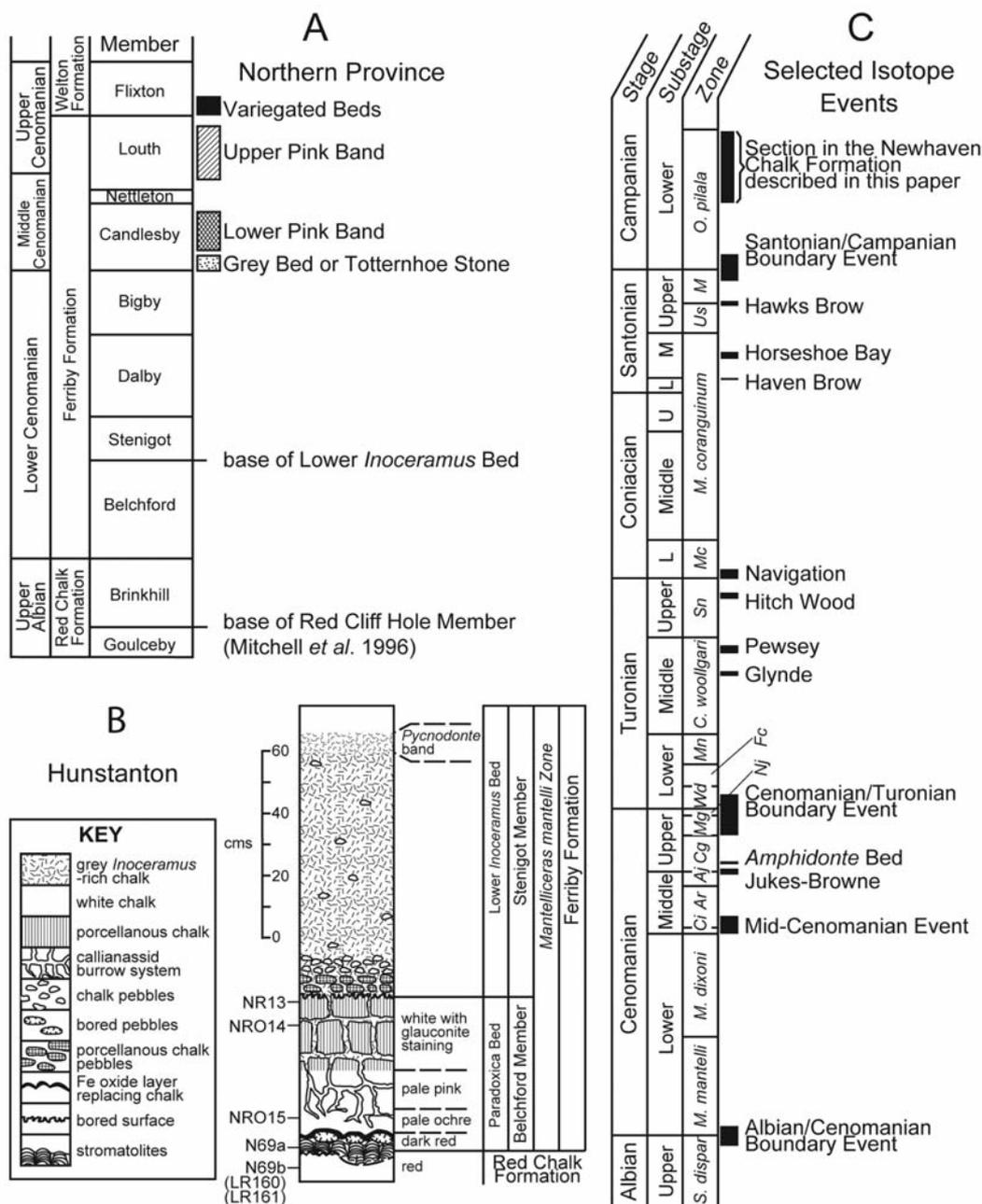
STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE

regard to the use of a  $\delta^{13}\text{C}$  carbonate reference curve as a primary criterion for correlation.

Locations mentioned are shown in Text-fig. 1.

The stratigraphical schemes and terms used are shown in Text-fig. 2.

The lithostratigraphical nomenclature used does not



Text-fig. 2. A. Stratigraphy of the upper Albian and Cenomanian chalks of the Northern Province after Wood and Smith (1978) and Jeans (1980). Various lithological units and horizons mentioned in the text are indicated. Some of the Chalk members (e.g. Louth, Nettleton) can be recognised in the Southern Province of England. B. Details of sample locations from the top of the Red Chalk and the overlying Paradoxica Bed at Hunstanton. Samples (LR160) and (LR161) are from the Red Chalk at Stenigot. C. Stratigraphical column showing the stages, sub-stages and palaeontological zones of the English Chalk in relation to various isotope events of Jarvis *et al.* (2006) mentioned in the text. The section of Newhaven Chalk Formation investigated in detail is indicated. Abbreviations: L – Lower, M – Middle, U – Upper; Ci – *Cunningtoniceras inerme*; Ar – *Acanthoceras rhotomagense*; Aj – *Acanthoceras jukesbrownei*; Cg – *Calycocheras guerangeri*; Mg – *Metoicoceras geslinianum*; Nj – *Neocardioceras juddii*; Wd – *Watinoceras devonense*; Fc – *Fagesia catinus*; Mn – *Mammites nodosoides*; Sn – *Subprionocyclus neptuni*; Mc – *Micraster cortestudinarium*; Us – *Uintacrinus socialis*; M – *Marsupites*; Op – *Offaster pilula*

necessarily follow the scheme of the British Geological Survey (Mortimore 2011, figs 2, 4). This applies to the Louth Member (Ferriby Formation) of the Northern Province and to the Holywell Nodular Chalk Formation of southern England. The Louth Member can be recognised in southern England as a prominent but unnamed unit within the Zig Zag Chalk Formation; this Northern Province term is applied to this unit in this paper. The Holywell Nodular Chalk Formation consists of two units, the Plenus Marls Member at the base and an unnamed unit of shelly and calcisphere-rich, often nodular chalk making up most of the formation; this unnamed unit is referred to as the Melbourn Rock Member.

## METHODS

The percentage weight of acid insoluble residues (AIR) in chalk samples were determined by two methods. Samples from the Newhaven Chalk Formation at Peacehaven Steps, Sussex, and from the Cenomanian Louth Member at Ballard Cliff, Dorset, were determined gravimetrically using 1 molar acetic acid and preweighed Whatman no. 42 filter paper to collect the AIR (Jeans 1980, p. 155 for details). Samples from the Holywell Nodular Chalk Formation at Eastbourne, Sussex, were analysed by the back titration method using standard volumetric 1 molar HCl for dissolution and back titration with standard volumetric 1 molar NaOH using Bromocresol Green as indication (Jeans 1980, p. 155 for details).

Trace element content (Fe, Mn) in the calcite of bulk samples of chalk from Ballard Cliff was determined with a Perkin-Elmer Absorption spectrophotometer (model 2280). Correction was made for the AIR in the analysis. Stable isotope analysis was performed at the Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge. Samples PHS1–65 were analysed for  $O^{16}/O^{18}$  and  $^{12}C/^{13}C$  of carbonates using either a Micro-mass 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 with reference to the VPDB and the precision was better than  $\pm 0.06$  per mil for  $^{12}C/^{13}C$  and  $\pm 0.6$  per mil for  $O^{16}/O^{18}$ . The acid insoluble residues of samples PHS1–52 were analysed for organic carbon and  $^{12}C_{org}/^{13}C_{org}$  values by continuous flow using a Costech Elemental Analyser attached to a Thermo Electron MAT 253 mass spectrometer. The results were calibrated to VPDB using inter-

national organic standards. The precision was better than  $\pm 0.05$  per mil.

The burial and palaeotemperature curve for the Newhaven Chalk Formation at Peacehaven has been derived from data in White (1921), Aubry (1986), Daley and Balson (1999), Hopson (2005) and Hopson *et al.* (2008) using Schlumberger's software PetroMod 11 ID Express.

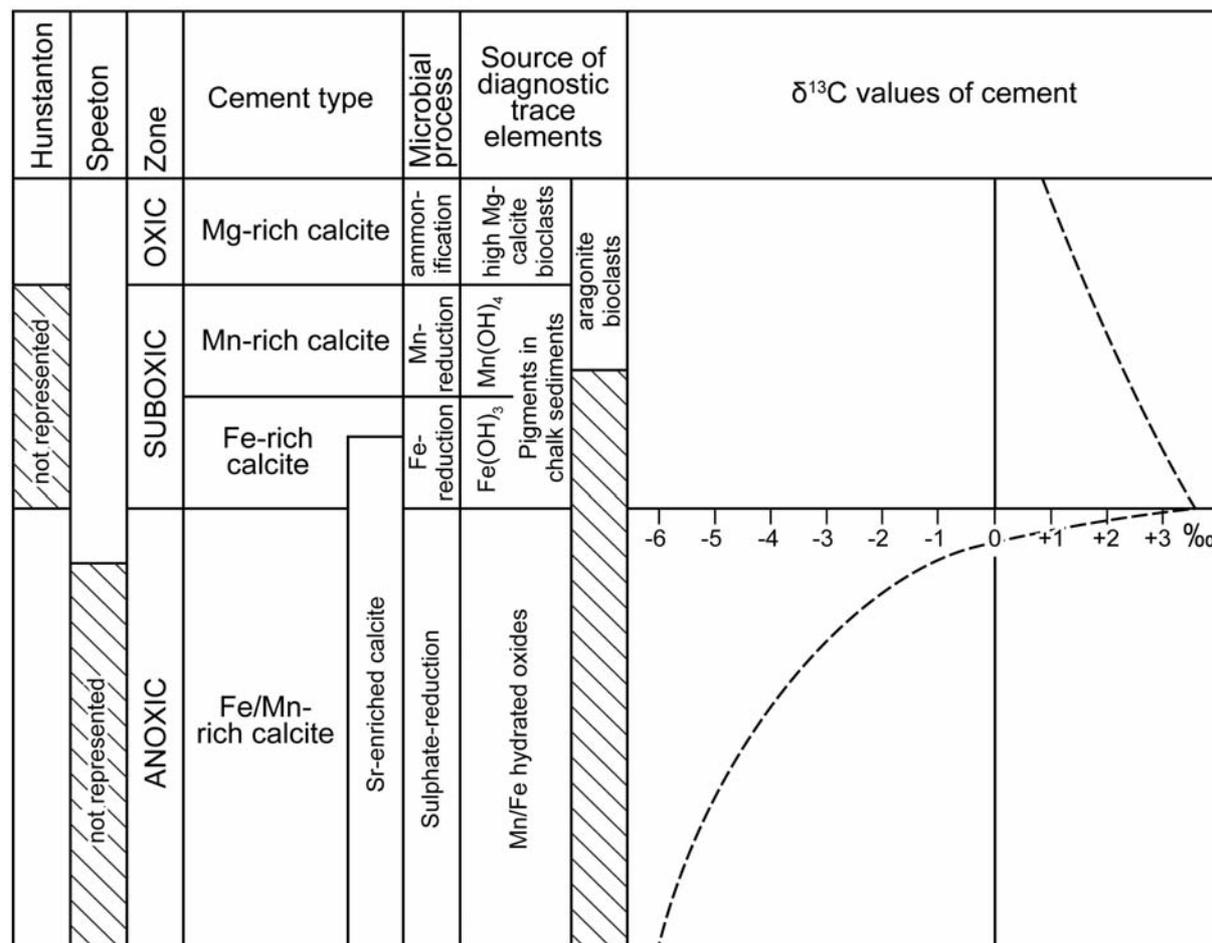
## GEOCHEMISTRY OF CHALK CEMENTS

Only recently has direct investigation of the geochemistry of the cementation process become possible. The fine-grained nature of the Chalk, dominated by the remains of Coccolithophoridae, is such that sufficiently large crystals of calcite cement are not generally available to determine the history of cementation. Recently, however, this was achieved for the calcite cements of the Cenomanian Chalk of eastern England by investigating the calcite cement infilling voids within the shell cavity of terebratulid brachiopods. Evidence demonstrates that the calcite filling has not come from allochthonous pore fluids penetrating the chalk and the well preserved brachiopods (valves tightly shut) through a fracture system, but is the result of precipitation from the Chalk's pore waters. The pattern of trace elements in the calcite cement from the voids inside the brachiopods can be matched with different types of lithification in the main mass of the Chalk (Hu, Long and Jeans, submitted). The results are summarised in Table 1. Two patterns, the suboxic and the anoxic series, are recognised in the geochemistry of the calcite cement (Text-fig. 3). The earliest cement in both series is Mg-rich, non-luminescing, and poor in Fe, Mn and Sr. A single stable isotope analysis shows it to have a positive  $\delta^{13}C$  value (0.58‰). Subsequent cements in the suboxic series are characterised by positive  $\delta^{13}C$  values which become increasingly heavier as cementation progressed, reaching values of 3.5‰. In contrast the anoxic series is characterised by negative  $\delta^{13}C$  values which become lighter as cementation progressed, reaching values as low as -6.5‰. The suboxic pattern of cementation is associated with the Upper Albian and Cenomanian chalks at Speeton, Yorkshire, where a fine-grained red hematite pigment is still present (Text-fig. 4) or has only been lost by late diagenetic sulphidization after the precipitation of the last phase of calcite cement recorded in the brachiopods. The anoxic pattern is associated particularly with hardground development linked to the precipitation of fine-grained glauconite and to the early diagenetic loss of the fine-grained red hematite pigment resulting from the development of anoxic pore water conditions through microbial activity (Text-fig. 3).

STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE

Paradoxica Bed, Hunstanton			Coloured Chalks, Speeton		
oxic cement	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰	no data	no data	oxic cement
	0.6	-5.3			
anoxic cement	-0.4	-7.5	1.1	-6.4	suboxic cement
	-1.4	-7.4	1.2	-6.7	
	-1.5	-8.2	1.3(4)	-4.9(4)	
	-2.1	-8.3	1.7	-6.1	
	-2.7(2)	-8.5(2)	2.1(4)	-7.3(4)	
	-5.6	-10.1	2.3	-7.4	
	-5.8	-8.3	2.6	-8.1	
	-6.6	-9.6	2.8(3)	-8.4(3)	
			2.9	-8.7	
		3.5	-7.6		

Table 1. Stable isotope values of calcite cements from the vugs preserved in the shell cavities of terebratulid brachiopods of east England. The  $\delta^{13}\text{C}$  analyses are arranged to reflect schematically (a) the increasing light values of the cements associated with the Paradoxica Bed as cementation progressed, and (b) the increasingly heavy values associated with cementation in the coloured chalks at Speeton. Figures in parentheses refer to the number of analyses with these values



Text-fig. 3. Schematic diagram summarizing the interpretation of the suboxic and anoxic cement series based upon the trace element and stable isotope patterns of the calcite-filled vugs in terebratulid brachiopods from the Cenomanian chalk of eastern England

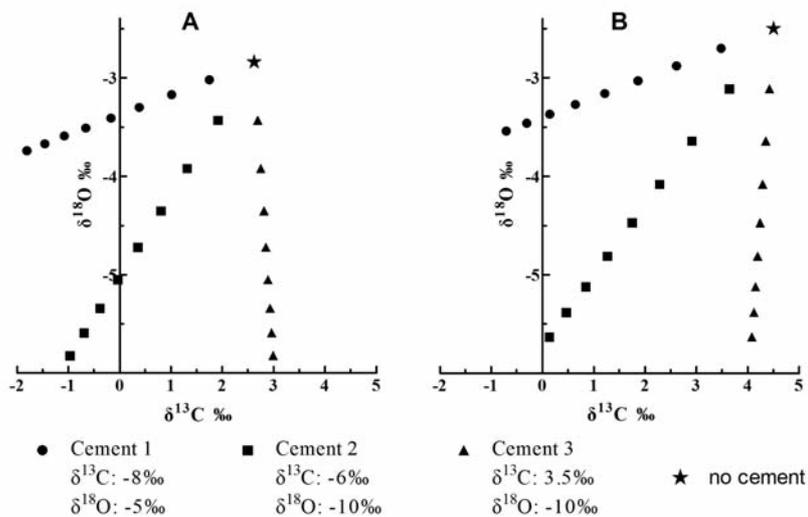


Text-fig. 4. Coloured chalk of Upper Albian age at Speeton, Yorkshire, UK. Nodular chalk of the Brinkhill Member (Ferriby Formation) with its uppermost unit (massive marl) at the top of the cliff section

MODELLING THE EFFECTS OF CEMENTATION

We use calcite cement of three different isotopic composition to model the effects of cementation on the

$\delta^{13}\text{C}/\delta^{18}\text{O}$  values of bulk samples of uncemented chalk (Text-fig. 5). The isotopic compositions are similar to the more extreme values actually recorded from vugs inside brachiopods (Table 1) as well as from the cement



Text-fig. 5. Stable isotope cross plots showing the effects of adding three cements of different isotopic composition in 5 % volume increments to the Standard A uncemented chalk with its 40 % porosity and stable isotope values of  $\delta^{18}\text{O}$  -2.84‰ and  $\delta^{13}\text{C}$  2.62‰ and to Standard B uncemented chalk with its 40 % porosity and stable isotope values of  $\delta^{18}\text{O}$  -2.50‰ and  $\delta^{13}\text{C}$  4.5‰

affecting the Campanian Chalk at Peacehaven Steps (see later). Suboxic diagenesis is represented by a late cement ( $\delta^{13}\text{C}$  3.5‰,  $\delta^{18}\text{O}$  -10‰) from the coloured chalk at Speeton. Anoxic diagenesis is represented by a late cement ( $\delta^{13}\text{C}$  -6‰,  $\delta^{18}\text{O}$  -10‰) from the Paradoxica Bed, Hunstanton and the cement ( $\delta^{13}\text{C}$  -8‰,  $\delta^{18}\text{O}$  -5‰) affecting the Campanian Chalk at Peacehaven Steps. The “uncemented” bulk chalk is that calculated for the unlithified chalk of the Cenomanian Louth Member at Dover, this having been used in modelling the general cement geochemistry of the Louth Member in eastern England. It is considered to be a fully compacted chalk unaffected by early lithification and any appreciable pressure dissolution; it is referred to as the **Standard Louth Chalk**. The bulk specific gravity is 1.65, the acid insoluble residue is 4 volume percent, the  $\text{CaCO}_3$  content is 56 volume percent and the porosity is 40 volume percent. Two bulk chalk models are used, one (A) representing the chalk sediment just prior to the start of the Cenomanian–Turonian  $\delta^{13}\text{C}$  Excursion with a bulk isotope value of  $\delta^{13}\text{C}$  2.62‰ and  $\delta^{18}\text{O}$  -2.84‰; the other (B) representing the chalk sediment at the peak of the Excursion with bulk isotope values of  $\delta^{13}\text{C}$  4.5‰ and  $\delta^{18}\text{O}$  -2.50‰.

Text-fig. 5 demonstrates the effects of filling the pore space of Standards A and B in increments of 5 per cent cement from 0 to 40 percent when all the pore space has been occupied. Of particular interest is that with the suboxic cement the original value of the bulk chalk is modified by only  $\pm 0.5\%$  depending upon whether we are dealing with a sediment (A) from just prior to the initiation of the Excursion or with one (B) from the peak of the Cenomanian–Turonian  $\delta^{13}\text{C}$  Excursion. In contrast the two anoxic cements have major effects on the  $\delta^{13}\text{C}$  values, with sediment (A) reaching  $\delta^{13}\text{C}$  values of -1‰ and -2‰, a difference of 3.6 to 4.6‰ from the original 2.62‰. Standard B shows a lightening of value from  $\delta^{13}\text{C}$  4.50‰ to  $\sim 0.0$  and -0.5‰, a difference of 4.5 – 5‰.

#### EFFECTS OF CEMENTATION ON THE $\delta^{13}\text{C}$ VALUES OF BULK CHALK

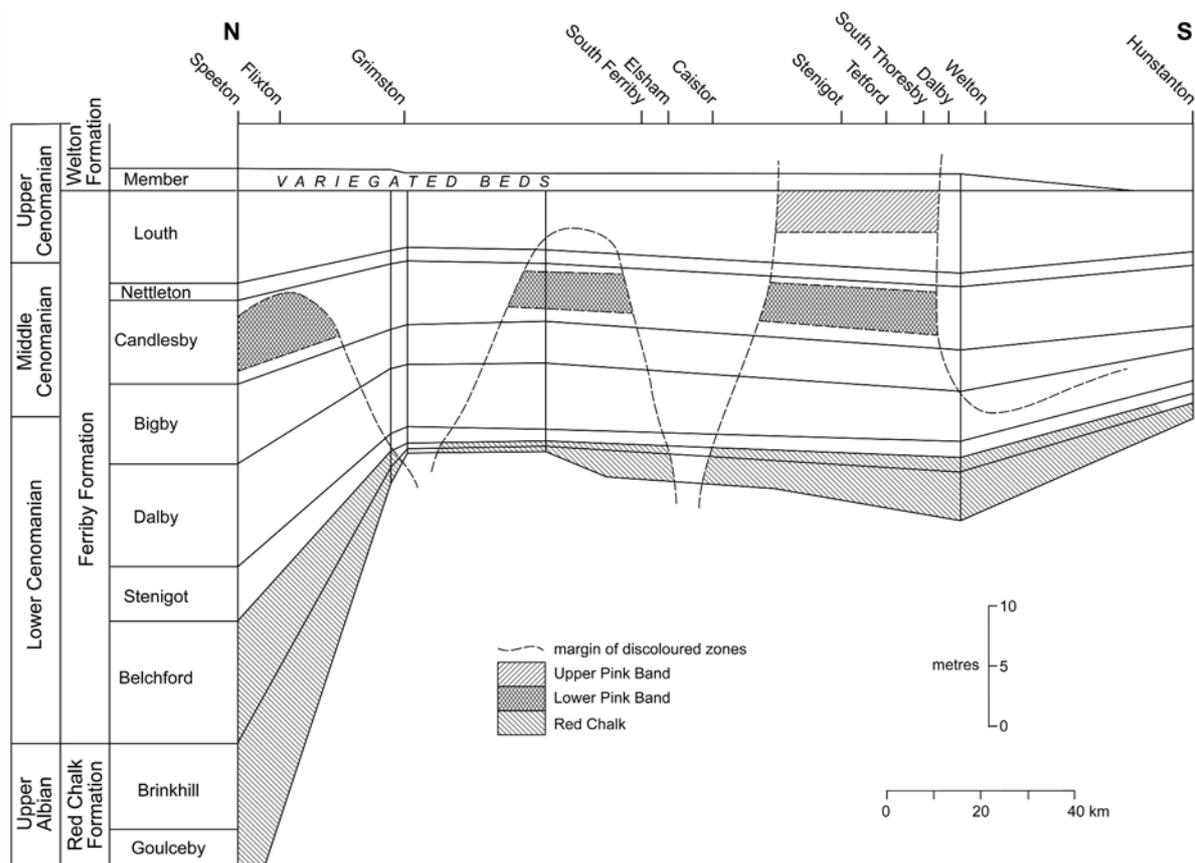
The isotope values for the cements used for modelling are the extreme but not exceptional values. The actual effect that a cement may have on the sediment will depend upon the average  $\delta^{13}\text{C}$  value for the bulk cement. It is quite conceivable that much of the cement has an extreme value. Our modelling has also used the uncemented **Standard Louth Chalk** with a conservative porosity of 40 volume percent. Other authors have suggested much higher porosities for the initiation of early

cementation (45–70%, Scholle and Kennedy 1974; 75–80%, Clayton 1986). This could result in much higher volumes of cement and this would enhance the degree to which a cement of a particular  $\delta^{13}\text{C}$  value could modify its host chalk. In this section the problem is approached from the opposite direction by taking actual stable isotope values of lithified chinks and modelling the composition of the cement whenever possible either by using the **Standard Louth Chalk** as the starting point or from observations of the degree of compaction between the uncemented and cemented states of the sediment.

#### ALBIAN AND CENOMANIAN CHALK OF EASTERN ENGLAND

Finely divided red hematite pigment is widespread in the Cenomanian and Upper Albian chinks and marls of eastern England. It is responsible for the red to pale pink to purple hues that colour these sediments. The presence of this pigment has proved to be a fairly reliable indicator that any calcite cementation which has taken place belongs to the suboxic series. Text-fig. 6 shows that in Norfolk, Lincolnshire and Yorkshire coloured chinks are restricted to four bands – the Upper Albian Red Chalk Formation and the basal part (Belchford Member) of the overlying Cenomanian Chalk; the Lower Pink Band of Bower and Farmery (1910) in the Candlesby Member (Middle Cenomanian); the Upper Pink Band of Bower and Farmery (1910) in the Louth Member (Upper Cenomanian), and in the Variegated Marls (Flixton Member, Upper Cenomanian–Turonian) of south Lincolnshire. At Speeton on the Yorkshire coast the hematite pigment occurs throughout the expanded sequence from the Red Chalk up to and including the Lower Pink Band, the only bed in this sequence that does not contain the hematite pigment is the Grey Bed at the base of the Candlesby Member.

The hematite pigment has been lost locally at two stages during the diagenesis of the Chalk. During early diagenesis the loss is associated with the development of hardgrounds and related types of lithification (Types 1 and 3, Jeans 1980); here the loss of pigment is associated with the precipitation of calcite cement of the anoxic series and the development of glauconite. Much later in diagenesis there is loss on a regional scale in zones that cross-cut the stratigraphy (Text-fig. 6) and this is associated with the precipitation of pyrite and marcasite; this post-dates the latest calcite cements recorded in the terebratulid brachiopods and is related probably to ascending anoxic, sulphide-rich, pore fluids penetrating the Chalk along basement faults.



Text-fig. 6. Horizontal section of eastern England showing the overall stratigraphy of the Upper Albian, Cenomanian and Lower Turonian strata and the general distribution of red colouration



Text-fig. 7. Fallen block at Hunstanton, Norfolk, UK, showing the inverted Paradoxia Bed and overlying grey Lower *Inoceramus* Bed (Text-fig. 2B). The upper part of the Paradoxia Bed contains uncompacted, chalk-filled callianassid burrows set in a well cemented chalk matrix. Portions of the dark red iron oxide layer (Text-fig. 2B) that has replaced the basal part of the Paradoxia Bed are present. Scale 5 cm

STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE

Type 1 lithification: Paradoxica Bed, Hunstanton							
	Sample no.	CaCO <sub>3</sub> wt%	Specific gravity	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰	model cement	
						$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰
Upper part	NR13	95	2.62	1.43	-1.88	0.52	-0.39
100mm below top surface	NRO14	96	2.31	1.40	-2.24	0.07	-0.97
400mm below top surface	NRO15	94	2.22	0.68	-3.73	-2.99	-6.24

Table 2. Calcium carbonate contents, specific gravity and stable isotope values used to model the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the cement in Type 1 lithification

Five types of early lithification and one phase of late lithification caused by calcite cementation at increasingly late stages of diagenesis have been recognised in the Upper Albian and Cenomanian chalks of eastern England (Jeans 1980). We will consider how five of these have or have not affected the  $\delta^{13}\text{C}$  values of the bulk chalk.

#### Type 1 lithification associated with hardground development

The Paradoxica Bed (Text-fig. 7; Jeans 1980, fig. 9; Gallois 1994, pl. 13) at the base of the Cenomanian Chalk in north Norfolk and its lateral extension throughout Lincolnshire and south Yorkshire is a particularly good example of hardground development (Jeans 1980). Its cementation history is known from Jeans (1980) and the investigation of the calcite-filled vugs preserved within its brachiopods (Table 1; Hu *et al.* 2012 this issue). Cementation must have started at the same time as or prior to the excavation of the branching *Thalassinoides* burrow system by callianassid crustaceans – this is at a much earlier stage of compaction than that used for the modelling exercise (see above). There is evidence that the original sediment contained  $\text{Fe}(\text{OH})_3$ , the assumed precursor to the hematite pigment, and this has been dissolved during lithification as the result of the development of anoxic conditions (Jeans 1980, fig. 22). Table 2 shows that the stable isotope values of the bulk calcite display a marked lightening of both the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values from the top bored surface downwards. The  $\delta^{13}\text{C}$  value of the bulk cement can be modelled by using the **Standard Louth Chalk** but with an initial value of 2.0‰, the approximate average  $\delta^{13}\text{C}$  derived from the data of Mitchell *et al.* (1996, fig. 5) for the red and pink stratigraphically equivalent chalks at Speeton from the base of his Red Cliff Hole Member to the base of the 1st *Inoceramus* Bed (Text-fig. 2A). The average  $\delta^{13}\text{C}$  of the modelled cement ranges from 0.52‰ at the top of the Paradoxica Bed to -2.99‰ at 400 mm below

the top surface. The equivalent values for  $\delta^{18}\text{O}$  are -0.39‰ and -6.24‰.

#### Type 2 lithification associated with algal-bound sediment

The calcite cement responsible for the lithification of algal-bound sediment at the top of the Red Chalk Formation (Upper Albian) at Hunstanton (Text-fig. 8) are enhanced in Mg, Mn and Fe (Jeans 1980, p. 108; Hu *et al.* 2012 this issue). Table 3 shows that the  $\delta^{13}\text{C}$  values of the red algal-bound sediment is 1.14‰ whereas the lithified crust, a pink chalky limestone, has a heavier value, 1.26–1.32‰. Corresponding values of  $\delta^{18}\text{O}$  are -3.63‰ for the algal-bound sediment and -2.71 to -2.89‰ for the lithified crust. Modelling the cement suggests it has values of  $\delta^{13}\text{C}$  1.4 to -2.4‰ and  $\delta^{18}\text{O}$  0.99 to -1.8‰, appreciably heavier than the original sediment.



Text-fig. 8. Polished vertical section through the top of the Red Chalk at Hunstanton, Norfolk, UK, showing the dark red laminated stromatolite layer overlying pink chalky limestone associated with lithification type-2. NR59

#### Type 4 lithification associated with large ammonites

Large ammonites occur in the nodular chalks of the Ferriby Formation at Speeton. They have enhanced Mg, Mn and Fe in their bulk calcite compared to the more marly matrix of the surrounding nodular chalk (Jeans 1980; Hu *et al.* accepted). This pattern of trace element enhancement is also seen in the calcite cements of

the suboxic series preserved in the shell cavities of terebratulid brachiopods from Speeton (Hu *et al.* 2012) where it is associated with increasingly more positive  $\delta^{13}\text{C}$  values. In spite of this the stable isotope values of the calcite from the ammonite chalk and the surrounding nodular chalk display no consistent pattern (Table 4), suggesting that the expected increase in  $\delta^{13}\text{C}$  values is masked by the local variability in the isotopic values of the chalk sediment.

### Type 5 lithification associated with nodular chalks

Much of the Cenomanian and Upper Albian section at Speeton consists of nodular chalks and nodular marls, most of which still retain a red hematite pigment (Text-fig. 9). Some of this pigment has been lost in sulphidization zones that cross-cut the stratigraphy. The sulphidization post-dates all stages of the calcite cements recorded by Hu, Jeans and Dickson (submitted) in the terebratulid brachiopods. The development of the nodularity has been caused by the precipitation of a calcite cement relatively enriched in Fe (Jeans 1980).

This cement represents the final phase (Fe-rich with the heaviest  $\delta^{13}\text{C}$  values) in the suboxic cementation series. Table 5 shows the stable isotope values of the bulk calcite of nodules and their matrices from a number of horizons at Speeton. Differences between the  $\delta^{13}\text{C}$  values of nodule/marl pairs range from 0.01 to 0.49‰, the equivalent values for  $\delta^{18}\text{O}$  are 0.12 to 0.99‰. There is no consistent pattern between nodule and adjacent matrix. The expected difference in  $\delta^{13}\text{C}$  values is obscured by local variations in the chalk sediment.

### Late lithification associated with pressure solution cementation

The late phase of calcite cementation associated with the development of pressure dissolution marl seams described from the Louth Chalk Member at Speeton (Jeans 1980, p. 89) displays a distinctive stable isotope pattern. Table 6 shows that the values for the marl seams are consistently heavier than those from the adjacent chalk. The  $\delta^{13}\text{C}$  values of the bulk calcite from the marls are on average heavier by 0.24‰ (range 0.15 to

Type 2 lithification: algal-bound sediment, Red Chalk Formation						Model cement	
	Sample no.	CaCO <sub>3</sub> wt%	Specific gravity	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰
						uncemented	
stromatolite layer	N69a	40	1.81	1.14	-3.63		
lithified chalky limestone	N69b	83	2.18	1.26	-2.89	1.44	-1.79
	LR160	92	2.23	1.33	-2.20	1.54	-0.62
	LR161	88	2.37	1.71	-1.54	2.40	0.99

Table 3. Calcium carbonate contents, specific gravity and stable isotope values used to model the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the cement in Type 2 lithification

Type 4 lithification: large ammonites					
Sample no.		$\delta^{13}\text{C}$ ‰	AI/NI	$\delta^{18}\text{O}$ ‰	AI/NI
A6	AI	2.74	0.96	-3.63	0.96
	NI	2.86		-3.79	
A5	AI	2.46	0.93	-3.55	1.02
	NI	2.64		-3.49	
A4	AI	2.52	0.91	-3.53	1.00
	NI	2.76		-3.54	
A7 (red)	AI	2.71	1.01	-3.21	0.94
	NI	2.67		-3.40	
A7 (grey)	AI	2.48	1.01	-3.46	0.96
	NI	2.46		-3.59	
A1	AI	2.17	1.01	-3.80	0.98
	NI	2.14		-3.87	

AI - ammonite interior; NI - nodule interior

Table 4. Stable isotope values and their ratios in the chalk associated with large ammonites and the adjacent nodular chalk in Type 4 lithification, Cenomanian Chalk, Speeton, Yorkshire, UK. Sample horizons are in Jeans 1980 (fig 16)

STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE



Text-fig. 9. Beds of red nodular chalk, Belchford Member (Ferryby Formation) at Speeton, Yorkshire, UK. In the upper bed pale pink nodules are set in a darker marly matrix, whereas in the lower bed this has been partly discoloured with the development of  $\text{FeS}_2$  minerals as the result of late-stage diagenesis (Text-fig. 6). Scale  $105 \times 150$  mm

Type 5 lithification: nodular chalks and marls					
Sample no.		$\delta^{13}\text{C} \text{ ‰}$	NI/matrix	$\delta^{18}\text{O} \text{ ‰}$	NI/matrix
F10	NI	2.74	0.96	-3.65	1.03
	matrix	2.85		-3.53	
F9	NI	2.60	0.98	-3.43	1.41
	matrix	2.66		-2.44	
F7	NI	1.90	1.04	-3.57	1.06
	matrix	1.83		-3.37	
F6	NI	2.19	1.12	-3.14	0.87
	matrix	1.95		-3.60	
F5	NI	2.18	1.07	-3.51	0.96
	matrix	2.04		-3.64	
F3	NI	2.10	0.95	-3.37	1.12
	matrix	2.20		-3.00	
F2	NI	2.16	0.82	-3.53	1.12
	matrix	2.65		-3.15	
F1	NI	2.38	1.00	-3.07	0.91
	matrix	2.37		-3.36	
NI - nodule interior					

Table 5. Stable isotope values and their ratios from nodular chalks and marls with Type 5 lithification, Cenomanian Chalk, Speeton, Yorkshire, UK. Sample horizons are in Jeans 1980 (fig. 16)

0.40‰) than the calcite from the adjacent chalk. The  $\delta^{18}\text{O}$  values are on average heavier by  $-1.63\%$  (range  $-0.60$  to  $-2.39\%$ ). The explanation is that the marl seams represent the original bioclastic values of the chalk sediment unaffected by the addition of calcite cement but modified by the selective loss of the finer calcite grains by pressure dissolution. The  $< 2\mu\text{m}$  fractions of chalk (mainly coccolith debris) usually have lighter  $\delta^{13}\text{C}$  than the rest of the sediment (Jeans *et al.* 1991, fig. 8) where they have been investigated in detail. Therefore the  $\text{HCO}_3^-$  in the pore solution from which cementation occurred in the adjacent beds of chalk is likely to have had a lower  $\delta^{13}\text{C}$  value and this is probably responsible for this systematic difference.

Late diagenetic pressure dissolution-related lithification			
Sample No.	$\text{CaCO}_3$ wt%	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰
R4	92	3.02	-4.60
Ysa39	49	3.14	-2.68
R3	99	2.94	-4.69
R9	89	2.93	-4.85
Ysa48	51	3.15	-3.39
Ysa29	54	3.14	-3.67
R8	87	2.82	4.55
R6	91	2.75	-4.18
Ysa47	50	3.15	-2.69
R1	95	2.86	-3.93
Ysa45	50	3.07	-3.33

R - chalk bed; Ysa - marl seam

Table 6. Stable isotope values associated with chalk beds and pressure dissolution marls, Cenomanian Chalk (Louth Member), Speeton, Yorkshire, UK. Sample horizons in Hu, Jeans and Dickson (in press)

## CENOMANIAN TO CAMPANIAN CHALKS OF SOUTHERN ENGLAND

Much of the evidence suggesting the presence of calcite cements of the anoxic series in the Cenomanian to Campanian Chalk of southern England is of a general nature and is based on comparison with the cement sequences and their associated diagenetic features revealed in the Cenomanian Chalk of eastern England. The most conspicuous feature is the complete lack of the red and pink hues that are associated with suboxic cements. Hardgrounds are not uncommon in the southern Chalk: these display all the geological features associ-

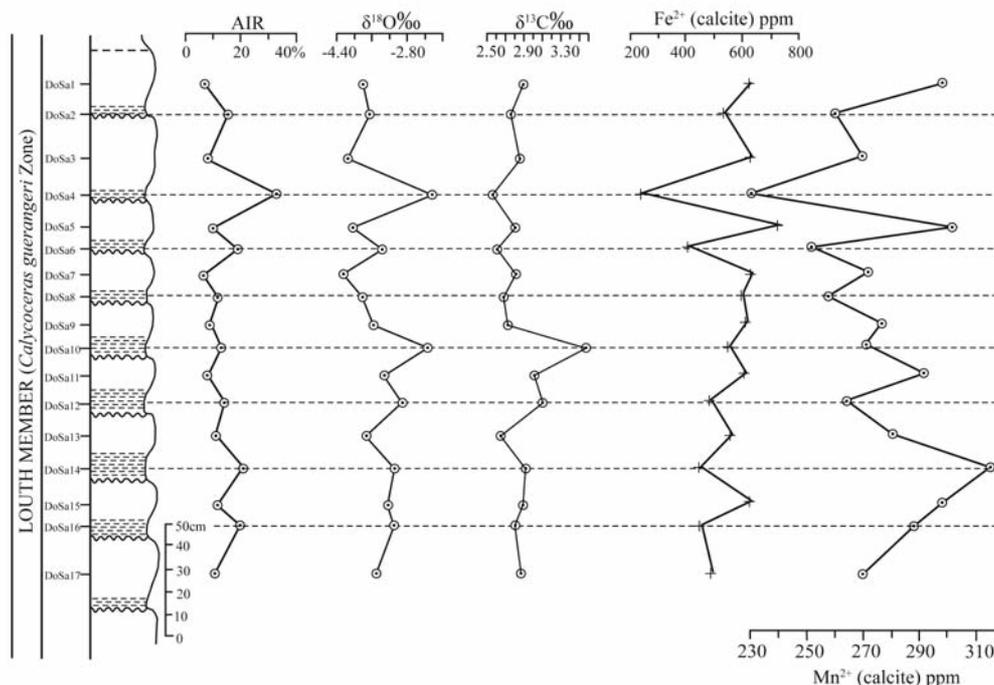
ated with the Paradoxica Bed in eastern England and it is probable that the southern hardgrounds are similarly associated with cements of the anoxic series and their negative  $\delta^{13}\text{C}$  values. The general observations of Scholle and Kennedy (1974) on the stable isotope values of hardgrounds in the English Chalk support this.

The presence throughout the Chalk of southern England of iron sulphide as pyrite, marcasite or as oxidised rusty nodules or stains commonly associated with fossils indicates anoxic conditions of diagenesis. Any calcite cement precipitated under these conditions would be expected to have negative  $\delta^{13}\text{C}$  values. Evidence of oxic cements ( $\delta^{13}\text{C}$  2.5–3.5‰) is provided by Mitchell *et al.* (1997) and Paul *et al.* (1999) in the Plenus Marls at Eastbourne and Dover. In contrast, from the same horizon and localities Voigt *et al.* (2006) suggest that the  $\delta^{13}\text{C}$  value of the bulk rock has been diagenetically lightened by 1.5 to 2‰ compared to the pristine calcite from rhyconellid brachiopods. Such a change would be caused by the addition of an anoxic cement to the bulk sediment. The calcite cement associated with paramoudra flint development is considered to have been formed at least partially under anoxic conditions (Clayton 1986). Anoxic cements have been suggested by Jenkyns *et al.* (1994) to be the cause of the lighter  $\delta^{13}\text{C}$  profile associated with the Turonian sequence at Dover which is 0.2‰ lighter than the equivalent sections in the Trunch and Banterwick boreholes and at Culver on the Isle of Wight (Jarvis *et al.* 2006). The 0.2‰ enhancement of the values of  $\delta^{13}\text{C}$  for the Cenomanian chalk at Speeton (Jarvis *et al.* 2006) compared to those in southern England suggests widespread anoxic cementation in the south.

## Chalk-marl alternations at Ballard Cliff and Eastbourne

Some idea of the complexity of the effects of cement precipitation on the  $\delta^{13}\text{C}$  values of chalk can be seen in the range of variation in stable isotopes and trace elements in sequences of interbedded marls and chalks.

Text-fig. 10 shows the alternating limestone-marl facies in the upper part of the Cenomanian sequence at Ballard Cliff, Dorset. Throughout the section there is a well-defined covariation between the acid insoluble residue, the Fe (calcite) concentration and the  $\delta^{18}\text{O}$  value of the bulk calcite. This suggests that the limestone units compared to the marl units have undergone preferential cementation by calcite enriched in Fe either at an enhanced temperature or under greater influence of meteoric water. The Mn (calcite) and the  $\delta^{13}\text{C}$  values display different patterns. In the lower part of the section (DoSa17 – DoSa13) the Mn

STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE

Text-fig. 10. Chalk-marl alternations in the Louth Member, Ballard Cliff, Dorset, UK, showing systematic variations in the total acid insoluble residue (AIR), Fe (calcite), Mn (calcite),  $\delta^{13}\text{C}$  (calcite) and  $\delta^{18}\text{O}$  (calcite)

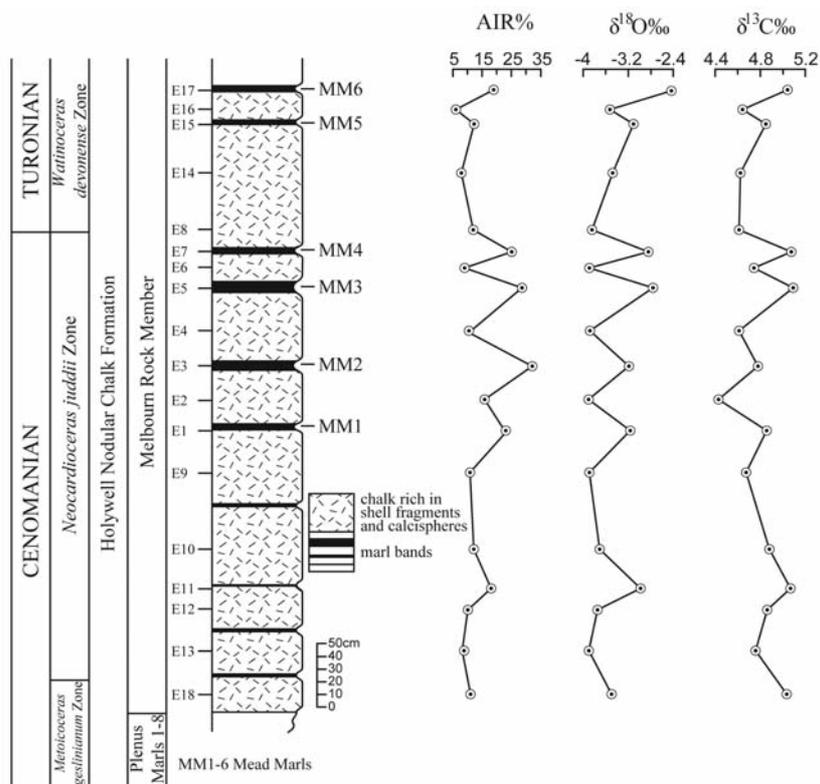
(calcite) pattern is independent of the limestone-marl alternations and the Fe (calcite) variation; such a relationship is recorded in the early stages of the suboxic cementation pattern when it is well preserved (Hu *et al.* 2012 this issue). Above this level the Mn (calcite) values covary with the Fe (calcite). The  $\delta^{13}\text{C}$  (calcite) values from the lowest three samples show no appreciable variation. This might suggest that the calcite cement associated with the two lowest limestones made no appreciable difference to their  $\delta^{13}\text{C}$  values. The next three alternations (DoSa14–DoSa9) have lighter  $\delta^{13}\text{C}$  in the limestones, indicating a lightening of the original value by the addition of an anoxic cement. The  $\delta^{13}\text{C}$  values for the four uppermost alternations (DoSa8–DoSa1) display the reverse relationship, with heavier values associated with the limestone units suggesting the effects of suboxic cementation. Similar complex patterns of Fe (calcite), Mn (calcite) and acid insoluble residues are known from the limestone-marl facies of the Cenomanian Chalk in the Isle of Wight, although stable isotope data is not yet available.

Text-fig. 11 shows a rather different style of limestone-marl alternations in the Melbourn Rock Member of the Holywell Nodular Chalk at Eastbourne. Here relatively thick, well cemented beds of chalk (20–95 cm thick) are separated by thin marl seams (5–80 mm

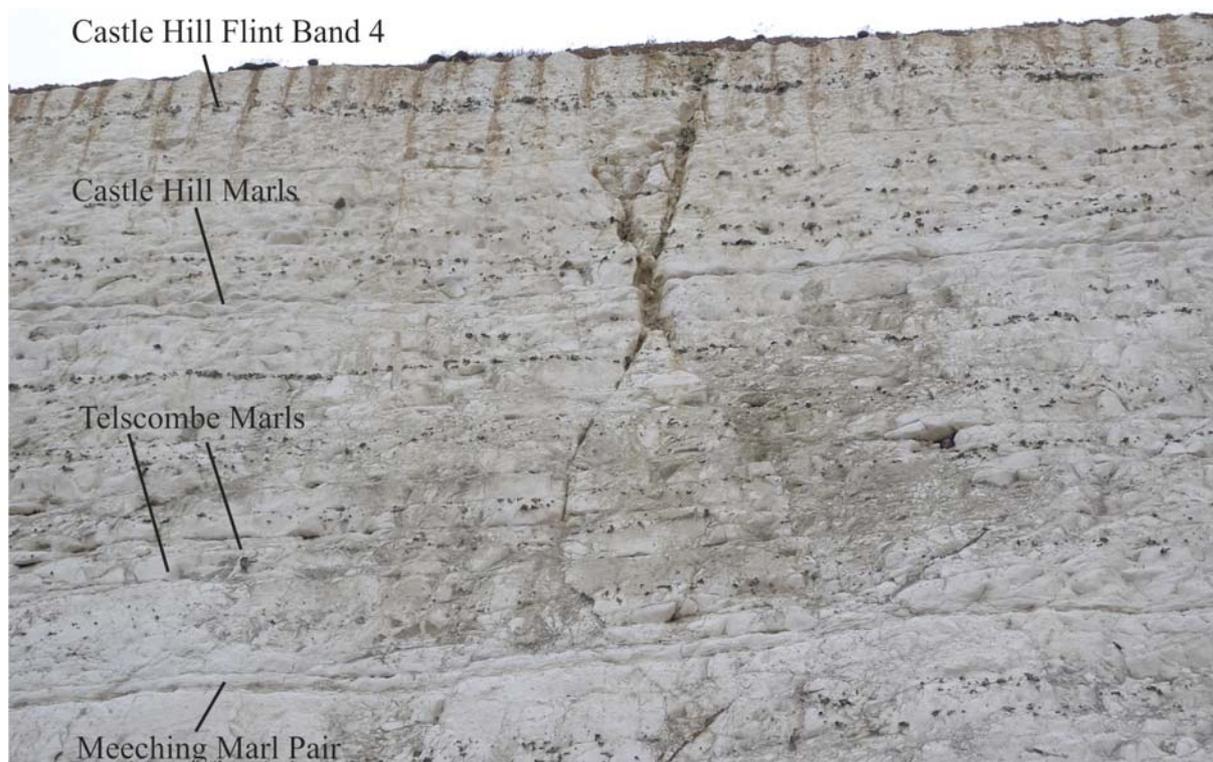
thick). The thicker and more persistent of these marls are referred to as the Meads Marls and are numbered 1 to 6. This section records the plateau of high  $\delta^{13}\text{C}$  values between 4.5 and 5 ‰ that constitutes part of the Cenomanian–Turonian  $\delta^{13}\text{C}$  Excursion at Eastbourne. Close correlation occurs between variations in acid insoluble residue and the stable isotope values of the bulk calcite, a relationship noted in part by Paul *et al.* (1999) in their detailed investigation of the Cenomanian–Turonian boundary section. The marls with their high acid insoluble residues have heavier  $\delta^{18}\text{O}$  (calcite) and  $\delta^{13}\text{C}$  (calcite) values relative to the chalk beds. This pattern of stable isotopes is similar to that described in an earlier part of this paper (late lithification associated with pressure dissolution cementation) and is considered to have the same origin.

#### Hard and soft chalk (*Offaster pilula* Zone) Newhaven Chalk Formation, Sussex.

The most direct evidence of anoxic cementation in the Chalk of southern England is an investigation of the pattern of variation in the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for a sequence of flinty white chalk of Early Campanian age (Text-figs 12, 13) at Peacehaven Steps on the Sussex coast which displays distinct variation in hardness. Samples were collected at 25 cm intervals throughout



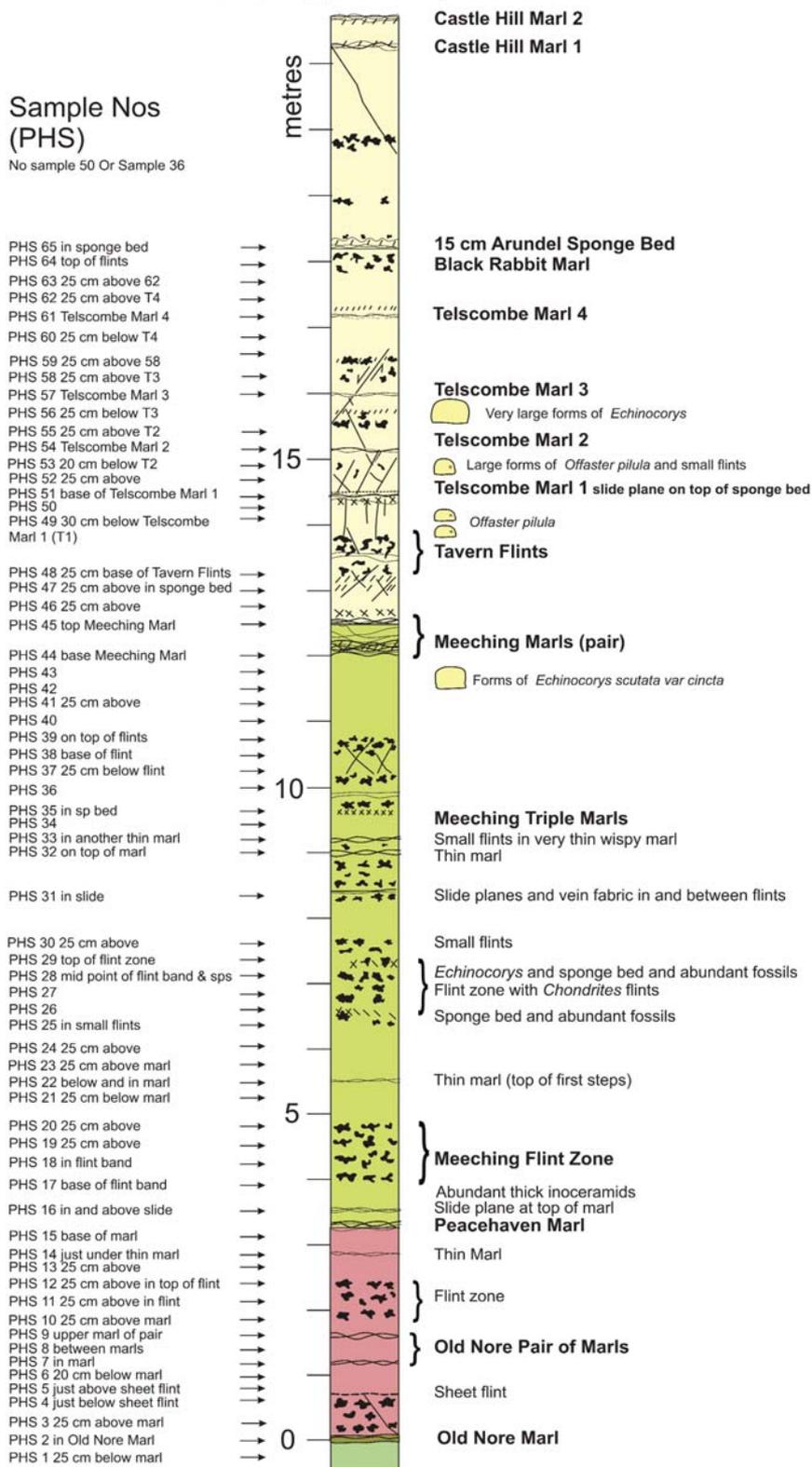
Text-fig. 11. Melbourn Rock Member (Upper Cenomanian–Lower Turonian) and Gun Gardens, Eastbourne, Sussex, UK, showing the pattern of variation in the total acid insoluble residue (AIR) and the stable isotope values ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) of the calcite in the bulk sediment



Text-fig. 12. Section in the *Offaster pilula* Zone (Lower Campanian) of the Newhaven Chalk Formation from the Meeching Marl Pair to above the Castle Hill Marls showing the alternation of flinty and non-flinty chalk and thin marl bands, near Peacehaven, Sussex, UK

STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE

Peacehaven Steps (PHS) Field Log 24th September 2008 and 12th August 2010



Text-fig. 13. Lithological section and sample horizons in the upper part of the Newhaven Chalk Formation (*Offaster pilula* Zone, Lower Campanian) at the Peacehaven Steps, Sussex, UK

the section. The isotopic values are shown in Table 7; their stratigraphic variation is shown in Text-fig. 14. Much of the section is characterized by variations in stable isotope values on a metre scale or less (Text-fig. 14). The  $\delta^{13}\text{C}$  values frequently vary by 0.4 to 0.5 ‰, the  $\delta^{18}\text{O}$  values by up to 0.9 ‰. These have no obvious correlation with lithology. The stable isotope patterns for the bulk calcite display a marked similarity between the variations in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. This suggests variation in the proportions of two types of chalk with different isotopic characters, one with relatively heavy  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, the other with relatively light values. More detailed investigation was carried out on 23 of the 63 samples. These samples were disaggregated in water by extended treatment in an ultrasonic bath. Five particle size fractions (<2  $\mu\text{m}$ , 2–8  $\mu\text{m}$ , 8–20  $\mu\text{m}$ , 20–40  $\mu\text{m}$ , 125–250  $\mu\text{m}$ ) were separated from 10 of these samples by a combination of sieving and differential settling (Stokes' formula) in slightly ammoniated water. For the remaining 13 samples (PHS 53–65) only the <2  $\mu\text{m}$  fraction was separated. The stable isotopes values of the bulk calcite of each separated fraction was determined (Table 8). The detailed results (Text-fig. 15) from the ten samples

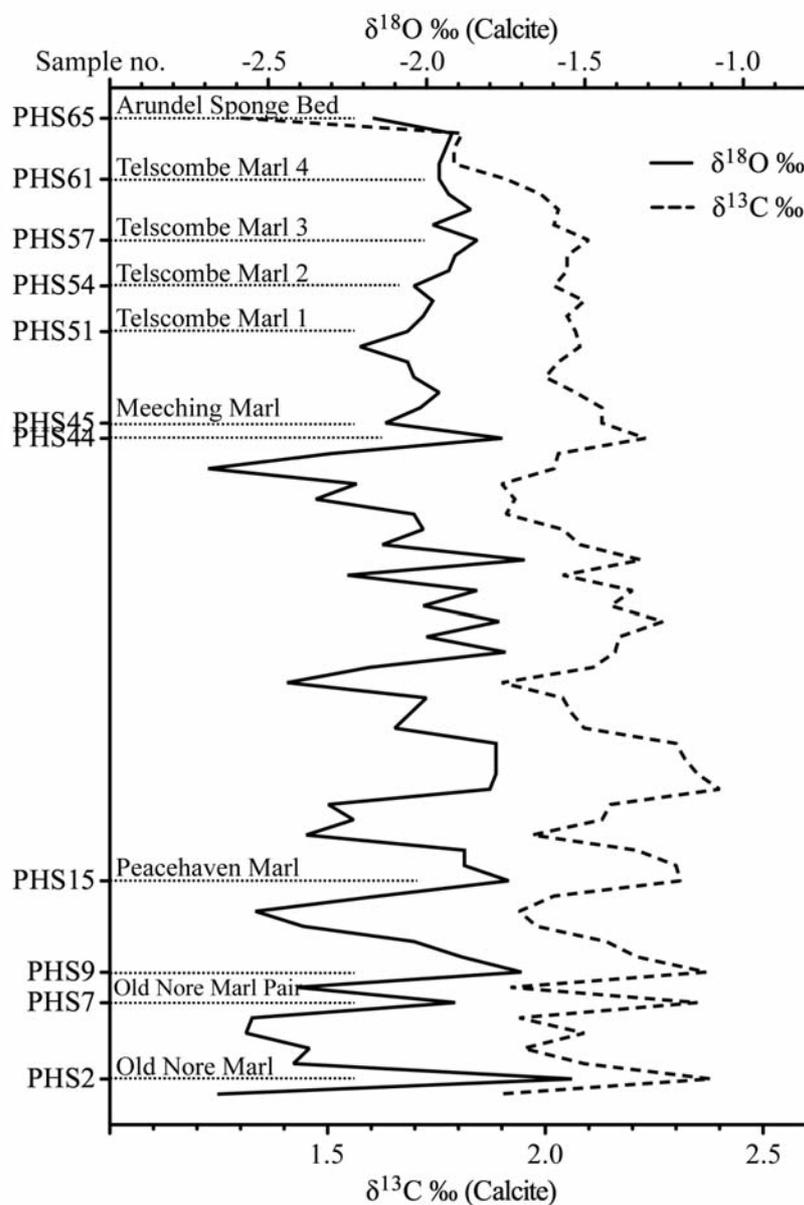
from the lower part of the section (0–13 metres) demonstrate that the values in the coarser fraction were little different from the total sample, but those from the <2  $\mu\text{m}$  fraction often showed very different values; these range for  $\delta^{13}\text{C}$  from 1.5 to –8‰ and for  $\delta^{18}\text{O}$  from –2 to –5‰.

The <2  $\mu\text{m}$  fractions from the top part of the section (PHS 53–65) display no such variation, with values little different than for the total sample. Text-fig. 16 is a cross plot of the stable isotope values for all the <2  $\mu\text{m}$  fractions. The close correlation between the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values is interpreted as the result of varying proportions of a two-component mixture consisting of original bioclastic material (probably mainly coccolith remains) with  $\delta^{13}\text{C}$  –2.3‰ and  $\delta^{18}\text{O}$  –1.8‰ and fine-grain particles of a cement with values at least as light as  $\delta^{13}\text{C}$  –8‰ and  $\delta^{18}\text{O}$  –6‰. Throughout the section with the anomalously light isotope values the weight percent of <2  $\mu\text{m}$  material separated from the disaggregated sample was surprisingly low (0.2–14 weight percent, averaging 3%), considering that much of this white chalk was expected to be the remains of coccoliths. This suggests a widespread cement precipitated under anoxic conditions. Assuming

Stable isotope values of bulk chalk, Peacehaven Steps, Sussex								
Sample	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰	Sample	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰	Sample	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰
PHS65	1.30	-2.17	PHS43	2.03	-2.30	PHS21	2.40	-1.80
PHS64	1.81	-1.92	PHS42	2.02	-2.69	PHS20	2.15	-2.31
PHS63	1.79	-1.94	PHS41	1.90	-2.22	PHS19	2.13	-2.23
PHS62	1.79	-1.96	PHS40	1.93	-2.35	PHS18	1.97	-2.38
PHS61	1.91	-1.96	PHS39	1.91	-2.04	PHS17	2.21	-1.88
PHS60	1.99	-1.93	PHS38	2.04	-2.01	PHS16	2.30	-1.88
PHS59	2.03	-1.86	PHS37	2.08	-2.14	PHS15	2.31	-1.74
PHS58	2.02	-1.98	PHS36	2.22	-1.69	PHS14	2.02	-2.15
PHS57	2.10	-1.84	PHS35	2.04	-2.25	PHS13	1.94	-2.54
PHS56	2.05	-1.91	PHS34	2.20	-1.84	PHS12	1.98	-2.39
PHS55	2.05	-1.93	PHS33	2.15	-2.01	PHS11	2.14	-2.04
PHS54	2.02	-2.04	PHS32	2.27	-1.77	PHS10	2.21	-1.89
PHS53	2.09	-1.98	PHS31	2.17	-2.00	PHS9	2.37	-1.70
PHS52	2.05	-2.01	PHS30	2.16	-1.75	PHS8	1.92	-2.41
PHS51	2.07	-2.06	PHS29	2.11	-2.18	PHS7	2.35	-1.91
PHS50	2.08	-2.21	PHS28	1.90	-2.44	PHS6	1.94	-2.55
PHS49	2.03	-2.06	PHS27	2.04	-2.00	PHS5	2.09	-2.57
PHS48	2.00	-2.04	PHS26	2.06	-2.05	PHS4	1.95	-2.37
PHS47	2.07	-1.96	PHS25	2.09	-2.10	PHS3	2.09	-2.42
PHS46	2.13	-2.02	PHS24	2.30	-1.78	PHS2	2.38	-1.54
PHS45	2.13	-2.13	PHS23	2.32	-1.78	PHS1	1.89	-2.66
PHS44	2.23	-1.76	PHS22	2.35	-1.78			

Table 7. Stable isotope values of samples PHS 1–65 from the Newhaven Chalk Formation (*Offaster pilula* Zone) at Peacehaven Steps, Sussex, UK

STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE



Text-fig. 14. Stratigraphical variation in the stable isotope values of 65 bulk chalk samples from the Lower Campanian section at Peacehaven Steps, Sussex, UK

the original marine porewaters were not diluted by freshwater or anoxic allochthonous porewaters leaking from depth the  $\delta^{18}\text{O}$  values of this cement indicate a minimum temperature of 35–40°C. A burial curve (Text-fig. 17) for the Newhaven Chalk Formation suggest a maximum depth of 1,000 metres and temperature of 62–68°C.

Additional evidence for the influence of anoxic calcite cement on the  $\delta^{13}\text{C}$  carbonate curve for the Peacehaven Steps section comes from comparing this with the curve for  $\delta^{13}\text{C}_{\text{org}}$  from the organic material within the

acid insoluble residues of samples PHS1–52 (Table 8). The amount of organic carbon in the residues range from 0.7 to 2.7%, averaging 1.65% by weight. The  $\delta^{13}\text{C}_{\text{org}}$  values range between –22 ‰ and –26 ‰, their stratigraphical variation shows an approximately antipathetic relationship to the pattern displayed by the  $\delta^{13}\text{C}$  values of carbonate. Assuming that the organic matter is derived from the changing faunas and floras that inhabited the Campanian sea during the deposition of the chalk sequence at Peacehaven Steps, this leaves no doubt that the  $\delta^{13}\text{C}$  carbonate curve is a diagenetic signal.

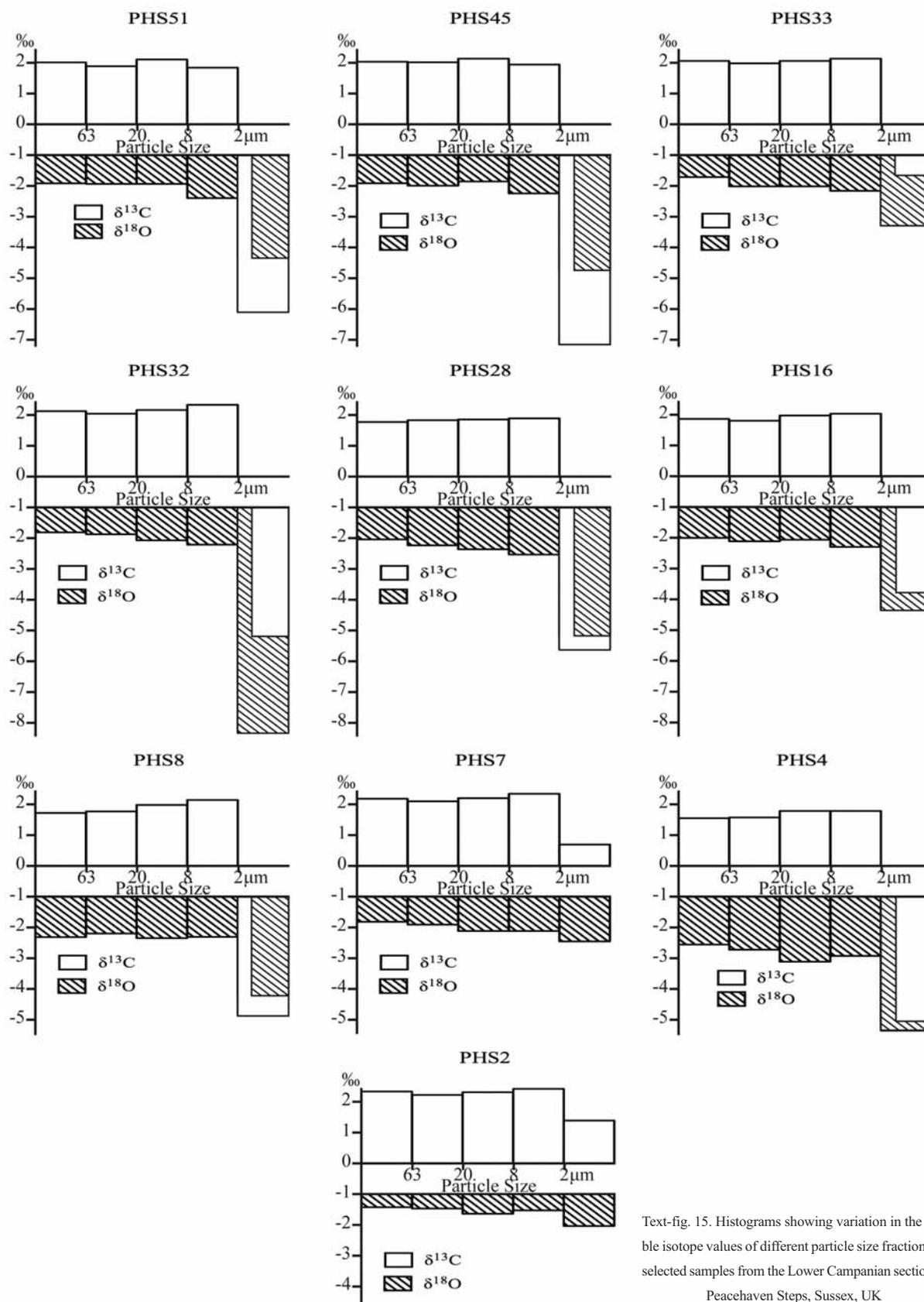
Sample	63-125 $\mu$ m		20-40 $\mu$ m		8-20 $\mu$ m		2-8 $\mu$ m		<2 $\mu$ m	
	$\delta^{13}\text{C}$ ‰	$\delta^{18}\text{O}$ ‰								
PHS65	-	-	-	-	-	-	-	-	1.57	-2.70
PHS64	-	-	-	-	-	-	-	-	2.05	-1.82
PHS63	-	-	-	-	-	-	-	-	2.05	-1.88
PHS62	-	-	-	-	-	-	-	-	2.21	-1.86
PHS61	-	-	-	-	-	-	-	-	2.26	-1.95
PHS60	-	-	-	-	-	-	-	-	2.23	-1.86
PHS59	-	-	-	-	-	-	-	-	2.30	-1.88
PHS58	-	-	-	-	-	-	-	-	2.31	-1.78
PHS57	-	-	-	-	-	-	-	-	2.13	-1.73
PHS56	-	-	-	-	-	-	-	-	2.12	-1.80
PHS55	-	-	-	-	-	-	-	-	2.11	-1.86
PHS54	-	-	-	-	-	-	-	-	2.21	-1.96
PHS53	-	-	-	-	-	-	-	-	2.00	-1.83
PHS51	2.01	-1.92	1.89	-1.94	2.11	-1.94	1.84	-2.40	-6.11	-4.35
PHS45	2.03	-1.92	2.01	-2.00	2.13	-1.86	1.94	-2.25	-7.16	-4.76
PHS33	2.06	-1.72	1.98	-2.02	2.06	-2.02	2.13	-2.17	-1.65	-3.29
PHS32	2.12	-1.82	2.04	-1.88	2.16	-2.08	2.33	-2.22	-8.33	-5.21
PHS28	1.77	-2.05	1.83	-2.24	1.85	-2.37	1.89	-2.54	-5.61	-5.18
PHS16	1.87	-2.00	1.81	-2.11	1.98	-2.06	2.04	-2.29	-3.77	-4.34
PHS8	1.73	-2.31	1.78	-2.19	1.99	-2.34	2.15	-2.30	-4.86	-4.20
PHS7	2.19	-1.81	2.11	-1.90	2.21	-2.11	2.35	-2.11	0.70	-2.45
PHS4	1.56	-2.55	1.58	-2.72	1.79	-3.11	1.79	-2.92	-5.03	-5.35
PHS2	2.34	-1.42	2.23	-1.46	2.32	-1.63	2.43	-1.52	1.40	-2.03

Table 8. Stable isotope values of separated particle size fractions from 23 samples from the Newhaven Chalk Formation (*Offaster pilula* Zone) at Peacehaven Steps, Sussex, UK

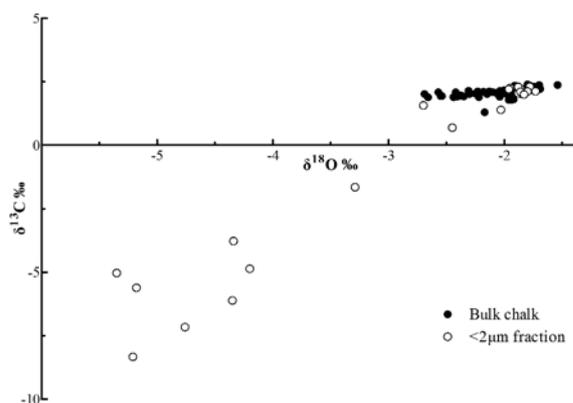
Stable isotope values of organic carbon							
Sample	$\delta^{13}\text{C}$ ‰	Sample	$\delta^{13}\text{C}$ ‰	Sample	$\delta^{13}\text{C}$ ‰	Sample	$\delta^{13}\text{C}$ ‰
PHS52	-24.5	PHS39	-24.8	PHS26	-25.3	PHS13	-24.5
PHS51	-24.0	PHS38	-24.8	PHS25	-25.0	PHS12	-23.6
PHS50	-25.1	PHS37	-24.7	PHS24	-25.7	PHS1 1	-24.9
PHS49	-24.3	PHS36	-23.3	PHS23	-26.0	PHS10	-24.1
PHS48	-24.0	PHS35	-23.0	PHS22	-24.9	PHS9	-23.8
PHS47	-24.1	PHS34	-24.1	PHS21	-24.5	PHS8	-22.4
PHS46	-24.7	PHS33	-23.8	PHS20	-24.0	PHS7	-24.0
PHS45	-25.1	PHS32	-24.5	PHS19	-24.0	PHS6	-24.0
PHS44	-24.6	PHS31	-25.1	PHS18	-24.6	PHS5	-24.6
PHS43	-23.8	PHS30	-24.8	PHS17	-24.8	PHS4	-24.1
PHS42	-23.8	PHS29	-24.4	PHS16	-24.6	PHS3	-24.5
PHS41	-24.2	PHS28	-24.8	PHS15	-24.3	PHS2	-23.1
PHS40	-23.8	PHS27	-23.9	PHS14	-25.1	PHS1	-23.9

Table 9. Stable isotope values ( $\delta^{13}\text{C}_{\text{org}}$ ) of the organic matter in samples PHS 1–52 from the Newhaven Chalk Formation (*Offaster pilula* Zone) at Peacehaven Steps, Sussex, UK

STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE



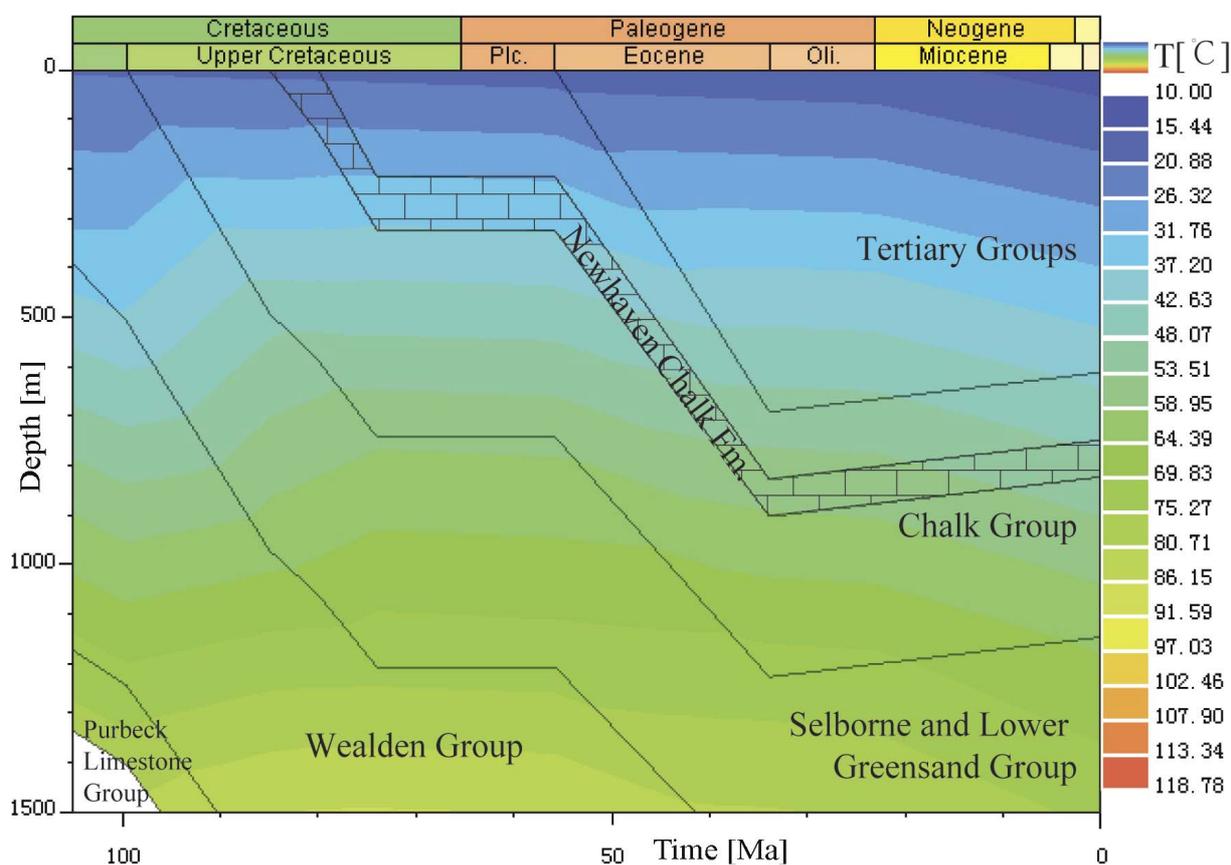
Text-fig. 15. Histograms showing variation in the stable isotope values of different particle size fractions of selected samples from the Lower Campanian section at Peacehaven Steps, Sussex, UK



Text-fig. 16. Cross plot of stable isotope values for (a) the 65 bulk chalk samples from Peacehaven Steps (Table 6), and (b) the  $<2\ \mu\text{m}$  fractions of 23 chalk samples from Peacehaven Steps (Table 7)

sequences of more and less hard chalk beds. Although Jarvis *et al.* (2006) did not include  $\delta^{18}\text{O}$  data to match their  $\delta^{13}\text{C}$  profile, the rapid variations in  $\delta^{13}\text{C}$  values for many of their Turonian, Coniacian and Campanian sequences suggest the effects of anoxic cements.

Indirect evidence of calcite cementation is given by bulk specific gravity values (SG) of chalk that can be measured in the laboratory (Jeans 1980, p. 155 for a method) and its comparison with “standard chalk” such as the one used for modelling the effects of cementation. Much information is to be found in the intact dry density (IDD = SG) and the P- and S-wave velocity profiles from boreholes that have been sunk for surveying the engineering properties of chalk in major road and tunnelling projects (Mortimore 2012).



Text-fig. 17. Burial curve for the Newhaven Chalk Formation at Peacehaven, Sussex, UK

## DISCUSSION

Patterns of stable isotope variations similar to those investigated at Peacehaven Steps are illustrated by Jenkyns *et al.* (1994, figs 6, 7) from the Santonian and Campanian strata at Seaford Head (Sussex) and the Campanian strata at Culver Cliff (Isle of Wight). We suggest that anoxic cementation is responsible for these

Text-fig. 18 shows the intact dry density and the P- and S-wave velocity profile as well as Poisson's Ratio, Young's Modulus, Bulk Modulus and Shear Modulus for part of the Newhaven Chalk Formation in two boreholes at Southwick Hill, 17 km from Peacehaven. The stratigraphic position of the section we investigated in some detail is shown. It spans a downhole increase in intact dry density from 1.63 to

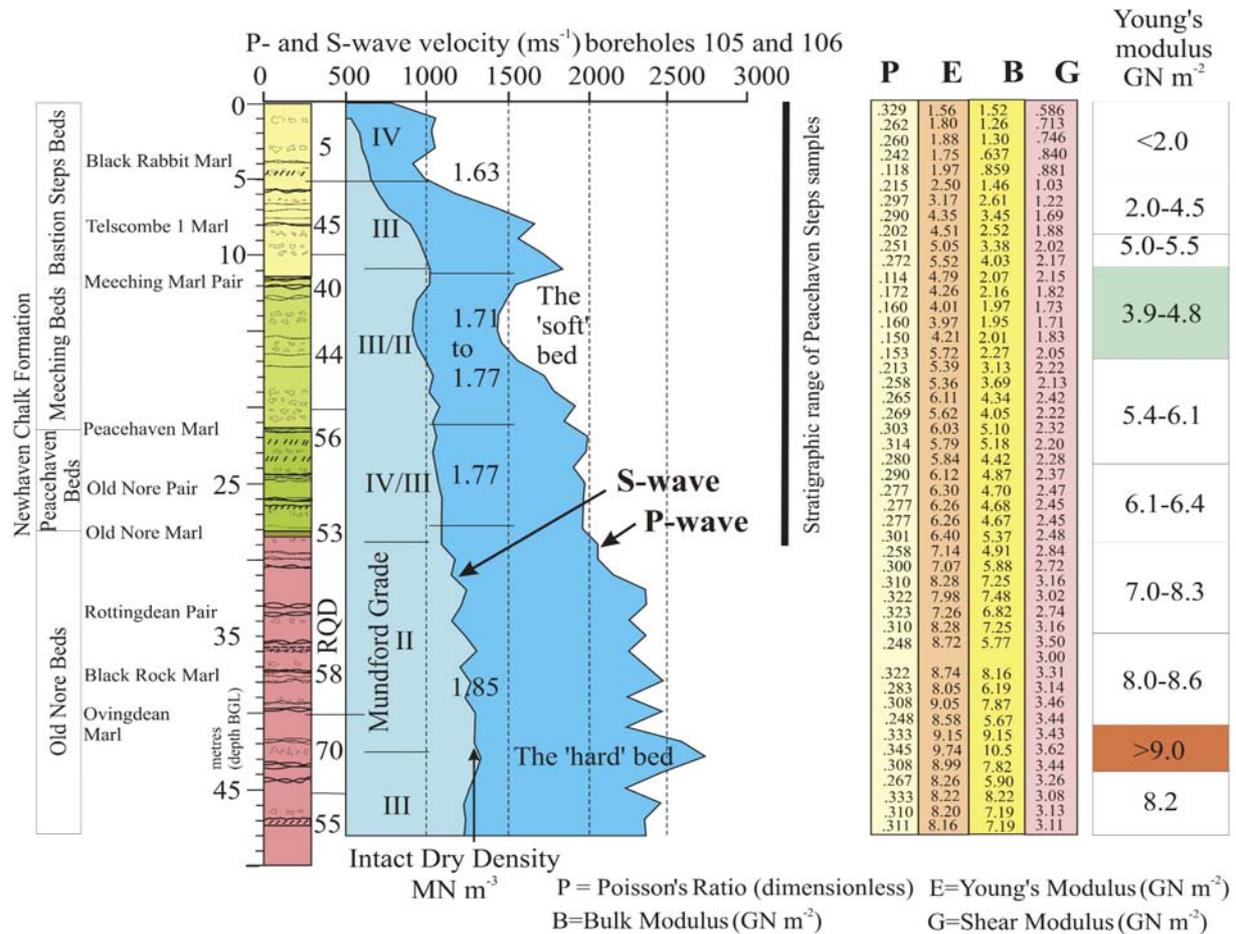
STRATIGRAPHICAL SIGNIFICANCE OF THE MARINE  $\delta^{13}\text{C}$  CARBONATE CURVE

1.85 with parallel increases in P and S wave velocities, Poisson's Ratio, Young's Modulus, Bulk Modulus and Shear Modulus. This matches our  $\delta^{13}\text{C}$  values from the  $<2\mu\text{m}$  fractions, with light values (down to  $-8\text{‰}$ ) first appearing at the approximate boundary between intact dry density values of 1.63 and 1.71–1.77. The geophysical log suggests that this zone of anoxic cementation extends at least 20 metres below the Old Nore Marl to the bottom of these boreholes.

It is clear that there is much to learn about the cementation history of the Chalk of southern England before the suitability of  $\delta^{13}\text{C}$  values from profiles of bulk chalk samples can be assessed for stratigraphical correlation. Direct measurement and modelling do not support the assumption that the  $\delta^{13}\text{C}$  values from southern England are closer to the palaeo-oceanographic signal than those from the coloured chinks of eastern England. Evidence indicates that the reverse is true, and that the southern values as a result of anoxic cementation have been lightened by 0.2‰.

The effects of calcite cementation upon the  $\delta^{13}\text{C}$  profile for the Cenomanian chinks at Speeton has

been relatively small. The absence of hardground development in this section (see Mitchell 1996 for alternative interpretation) and the systematic investigation of calcite-filled vugs within terebratulid brachiopods indicates calcite cements were suboxic with positive  $\delta^{13}\text{C}$  values throughout. The only exception is the Grey Bed (Middle Cenomanian) at the base of the Candlesby Member (Ferriby Formation) where negative  $\delta^{13}\text{C}$  values develop during the later stages of cementation. The presence of glauconite and the absence of finely divided hematite pigment in spite of its presence in the beds immediately above and below suggests that it was dissolved under anaerobic conditions during early diagenesis. Early lithification by the precipitation of cements with positive  $\delta^{13}\text{C}$  values have had no noticeable affect upon the bulk  $\delta^{13}\text{C}$  value of the original sediment. However, at a later stage of diagenesis, pressure dissolution and its associated cement precipitation in the upper part of the Louth Chalk Member have caused systematic changes in the  $\delta^{13}\text{C}$  pattern between the beds of chalk in which the new cement was precipitated and the beds now



Text-fig. 18. Burial curve for the Newhaven Chalk Formation at Peacehaven, Sussex, UK

preserved as marl seams from which it has been derived by the selective dissolution of the bioclastic components. The effects of this pressure dissolution/cementation are differences in  $\delta^{13}\text{C}$  values ranging from 0.15 to 0.40 ‰ (averaging 0.24‰), suggesting that the Jukes-Browne and *Amphidonte* Bed Isotope events which are defined by differences of no more than 0.13‰ may be diagenetic blips in the  $\delta^{13}\text{C}$  record.

Isotope events (e.g. Hitch Wood, Pewsey and Glynde events (Turonian); Navigation Event (Turonian–Coniacian); Santonian–Campanian Boundary Event) associated with hardground development and glauconite have to be assessed in the light that they are likely to have been affected by the precipitation of varying proportions of anoxic calcite cements comparable to that in the Paradoxica Bed in eastern England. Much of the variation between locations and within a single location may be the effect of this.

Inflection points in the  $\delta^{13}\text{C}$  reference curve at which the trend of  $\delta^{13}\text{C}$  values change, such as the Hawks Brow Event (Santonian), Horseshoe Bay Event (Santonian), Haven Brow Event (Santonian) and the Navigation Event (Turonian–Coniacian), may represent the points at which the style of calcite cementation changes. For example, the change from a cementation pattern with an increasing proportion of anoxic cement to one where the proportion of suboxic cement increases would change a trend to lighter bulk  $\delta^{13}\text{C}$  to one with heavier values, in spite of there being no change in the original oceanographic isotope values.

## CONCLUDING COMMENTS

The assumption that a bulk carbonate  $\delta^{13}\text{C}$  reference curve could be a stand-alone criterion for trans-continental correlation is based upon the premise that the  $\delta^{13}\text{C}$  values in the Upper Cretaceous Chalk of England have been little affected by diagenesis. Jarvis *et al.* (2006) consider the Chalk successions of England to be diagenetically immature. Unfortunately this is not correct in spite of the Chalk's superficial appearance of being little altered or even cemented. For 65–100 Ma the Chalk has undergone diagenesis. Most of the changes have been involved with miagenesis (Jeans 1984 for definition of diagenesis, miagenesis and metamorphism) and these have provided the fundamental differences that are related to the original depositional setting on the seafloor within the Late Cretaceous sea. Miagenesis refers to the group of mineralogical and chemical reactions occurring within and between the organic and inorganic components of a sediment, its pore fluids and its living biota

that take place at normal earth-surface temperatures. These reactions represent the development of a general chemical equilibrium between the components of the sediment and its pore fluids. The concept differentiates within diagenesis between the reactions related to metamorphism – the changes controlled essentially by temperature, pressure and stress – from those that are intrinsic to a sediment.

If the English Chalk can be referred to as diagenetically immature it can only refer to that part of its diagenesis related to metamorphism. There are obvious regional differences in cementation from soft friable chalk to hard micritic chalky limestone. These reflect the degree of metamorphism and are related to pressure dissolution under different stress situation. Other than the redistribution of dissolved  $\text{CaCO}_3$  to precipitate at other sites within the Chalk they have had only a relatively minor effect on the original miagenetic patterns. For example, the Cenomanian Chalk of eastern England is a chalky limestone caused very largely by the lithification of soft chalk by pressure dissolution-derived cements. In them are preserved evidence of the intrinsic patterns of suboxic and anoxic cementation. In contrast, the White Chalks of southeast England are soft and friable; in spite of the lack of obvious cementation, they have undergone just as extensive miagenetic modification as the better cemented and coeval sediments in eastern England. What is recorded in the  $\delta^{13}\text{C}$  record of the English Chalk is a record derived from an original palaeo-oceanographic signal affected to a greater or lesser extent or even obscured by a cementation signal. All the 72 isotope events described by Jarvis *et al.* (2006) from the Cenomanian–Campanian Chalk sections of England are of a magnitude that could be explained by the effects of calcite cementation – some even by localised variations in  $\delta^{13}\text{C}$  values at a single horizon of nodular chalk. With few exceptions (e.g. Albian–Cenomanian boundary Event, Mid–Cenomanian Event, Cenomanian–Turonian Anoxic Event) the majority of these events are defined by very modest changes in  $\delta^{13}\text{C}$  values when compared to those that have been shown to be of diagenetic origin. Until this is sorted out – and it will involve a lot of detailed investigation including the publication of the corresponding  $\delta^{18}\text{O}$  curves to allow geologists to draw their own conclusions – biostratigraphy will reign supreme in Upper Cretaceous correlation. Even with the major  $\delta^{13}\text{C}$  events that may represent widespread changes in the Late Cretaceous oceans, detailed biostratigraphy is the prime evidence because anoxic calcite cements can modify and obscure these events, even the Cenomanian–Turonian  $\delta^{13}\text{C}$  Event.

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