

# Redox conditions in the Late Cretaceous Chalk Sea: the possible use of cerium anomalies as palaeoredox indicators in the Cenomanian and Turonian Chalk of England

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## ABSTRACT:

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The cerium anomalies preserved in the Chalk have been investigated as possible palaeoredox indicators of the Late Cretaceous Sea and its sediment. This has been based upon over a hundred new rare earth element analyses of selected samples and grain size fractions from the Chalk. Particular attention has been given to the methodology of differentiating between the cerium anomalies preserved in the bioclastic calcite and those in carbonate-fluorapatite preserved in the acetic acid insoluble residues of chalks. Variations in the cerium anomaly of different particle size fractions of uncemented chalks suggest that fractionation of rare earth elements between the Chalk's seawater and the various organisms that contributed skeletal material to the bioclastic calcite of the Chalk may have occurred. Post-depositional processes of calcite cementation and late diagenetic sulphidisation have had no apparent effect on the cerium anomaly of the acetic acid insoluble residues. The cerium anomalies associated with the acetic acid insoluble residues from (1) an alternating sequence of chalks and marls from Ballard Cliff (Dorset, UK) typical of Milankovitch cyclicity show a marked diagenetic pattern, whereas those from (2) non-volcanic and volcanic marls display a pattern that is best explained by the variations in the availability of phosphorus and the timing of argillisation of volcanic glass during diagenesis. The general conclusion is drawn that the cerium anomalies preserved in the Chalk can provide an insight into the changing palaeoredox conditions in the Late Cretaceous Sea as well as in the pore fluids of its sediments.

**Key words:** Chalk environments; Rare earth element (REE) anomalies; Methods; Palaeoredox indicators; Diagenesis; History.

## INTRODUCTION

The changing redox conditions – that is the availability of oxygen – within the Late Cretaceous Chalk

Sea and its sediments must have played an important role in influencing the nature of the European Chalk as it is preserved today after 60–100 million years of diagenesis. Not only did the changing redox conditions

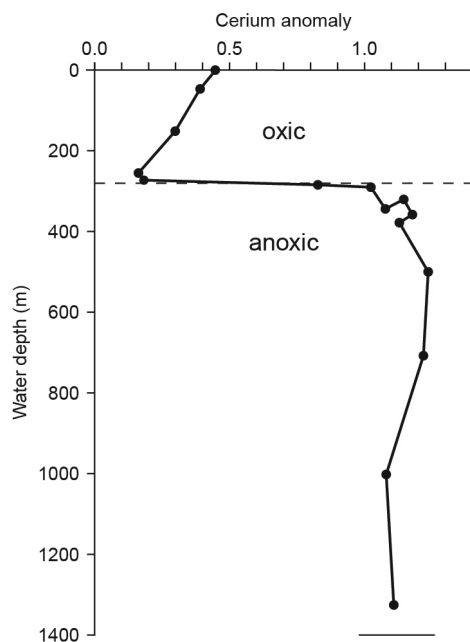
influence the faunas and floras that lived within the water column and on the seafloor but they also affected post-depositional processes – the preservation of organic matter, the varieties of calcite cement, and, the types of authigenic clay and iron minerals. Of particular interest has been the problem of the changes in the fossil faunas and floras that were widespread at certain times in the Chalk Sea, such as those associated with the Cenomanian–Turonian Anoxic Event. Do they reflect changes in the physical and chemical conditions of the sea or were they the result of invasions, unrelated to such changes, by more successful populations of new species? Comparison with the habitat of similar modern species may suggest an answer. An idea of the temperature and salinity can be gained from the stable oxygen isotope ratios of fossil groups (belemnites, brachiopods, bivalves, foraminifera, coccoliths) preserved in the Chalk (e.g. Jeans *et al.* 1991; Voigt *et al.* 2003) and possibly by the use of other proxies that are applied to foraminifera in the study of the recent history of oceans (Mg/Ca ratios – Sadekov *et al.* 2014, Hönisch *et al.* 2013; Sr/Ca ratios – Mortyn *et al.* 2005; U/Ca ratios – Yu *et al.* 2008; B/Ca ratios – Yu *et al.* 2007) as long as post-depositional change has not modified or destroyed the record. Some indication of the chemistry of the environment in the Chalk Sea can be gained from the varying trace element composition in the calcite skeletons of fossil organisms (e.g. Jeans *et al.* 1991) as well as from studies (e.g. Blumenberg and Wiese 2012)

of the organic geochemistry and biomarkers within the organic fraction. A method of particular promise that has not been applied in reconstructing the palaeoredox conditions in the Chalk is that proposed by German and Elderfield (1990); this is based on studies of the pattern of rare earth elements in the present oceans. These authors suggested that the patterns of rare earth elements preserved within (a) the skeletal material of organisms living within the present oceans and (b) authigenic minerals formed within the sediments can be used as a palaeoredox record with some degree of confidence as long as four ground rules are satisfied.

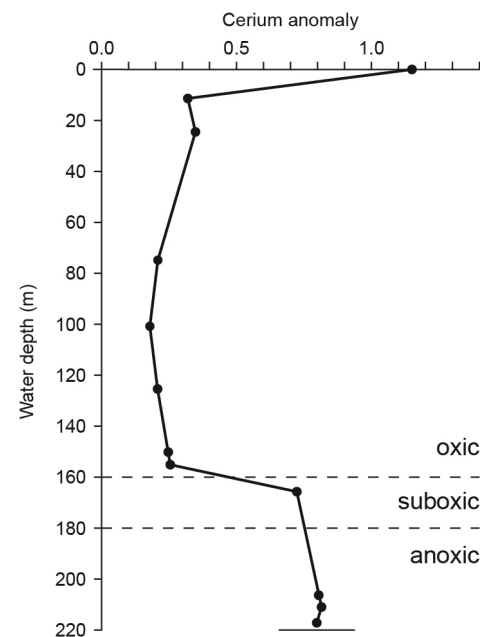
This method is based upon the exceptional chemical properties of the rare earth element cerium (Ce) in that (1) it can readily undergo oxidation from the solvated  $3^+$  state to the insoluble Ce (IV), and (2) the fractionation of cerium relative to the other strictly trivalent rare earth elements can only be affected by redox processes. The normalisation of the measured cerium abundances to those of the rare earth element series allow the extent of the oxidative removal of cerium from solution to be deduced—this is referred to as the cerium anomaly (Ce\*). Studies of the present oceans demonstrate that the cerium anomaly is a sensitive measure of the redox conditions.

The four ground rules of German and Elderfield (1990) are listed below. They underlie the use of the cerium anomaly as a palaeoredox proxy and are therefore of relevance to the study of the Chalk Sea.

### Cariaco Trench



### Saanich Inlet



Text-fig. 1. The relationship between the cerium anomalies, redox conditions and depth in the ocean waters at Saanich Inlet (after German and Elderfield 1989) and the Cariaco Trench (after de Baar *et al.* 1988)

1. *The oxidation state of cerium in seawater should respond in a predictable manner to redox conditions in the water column.* Studies in present oceans (e.g. Cariaco Trench, de Baar *et al.* 1988; Saanich Inlet, German and Elderfield 1989; N.W. Indian Ocean, German and Elderfield 1990) show that all rare earth elements are enriched under suboxic and anoxic conditions but cerium is preferentially enriched (Text-fig. 1).

2. *The negative/positive cerium anomaly measured in seawater should represent an instantaneous record of the oxic/anoxic conditions in the water column at the time the rare earth elements are incorporated into the relevant solid phase.* German and Elderfield (1990) conclude that cerium appears to undergo progressive oxidative removal from the deep oceans during the ageing of individual water masses. Thus the cerium anomaly in any seawater sample may only represent an integrated record of the redox history of that particular water mass.

3. *The cerium anomaly recorded by the solid phase should be related to that of the seawater source in a predictable manner.* German and Elderfield (1990) observe there is some evidence that fractionation of rare earth elements takes place between seawater and the rare earth elements incorporated into the calcite shells of foraminifera. The extent to which this has occurred between the Chalk's seawater and the calcite skeletons of organisms that inhabited it, is an important aspect in assessing the significance of the cerium anomaly in the Chalk.

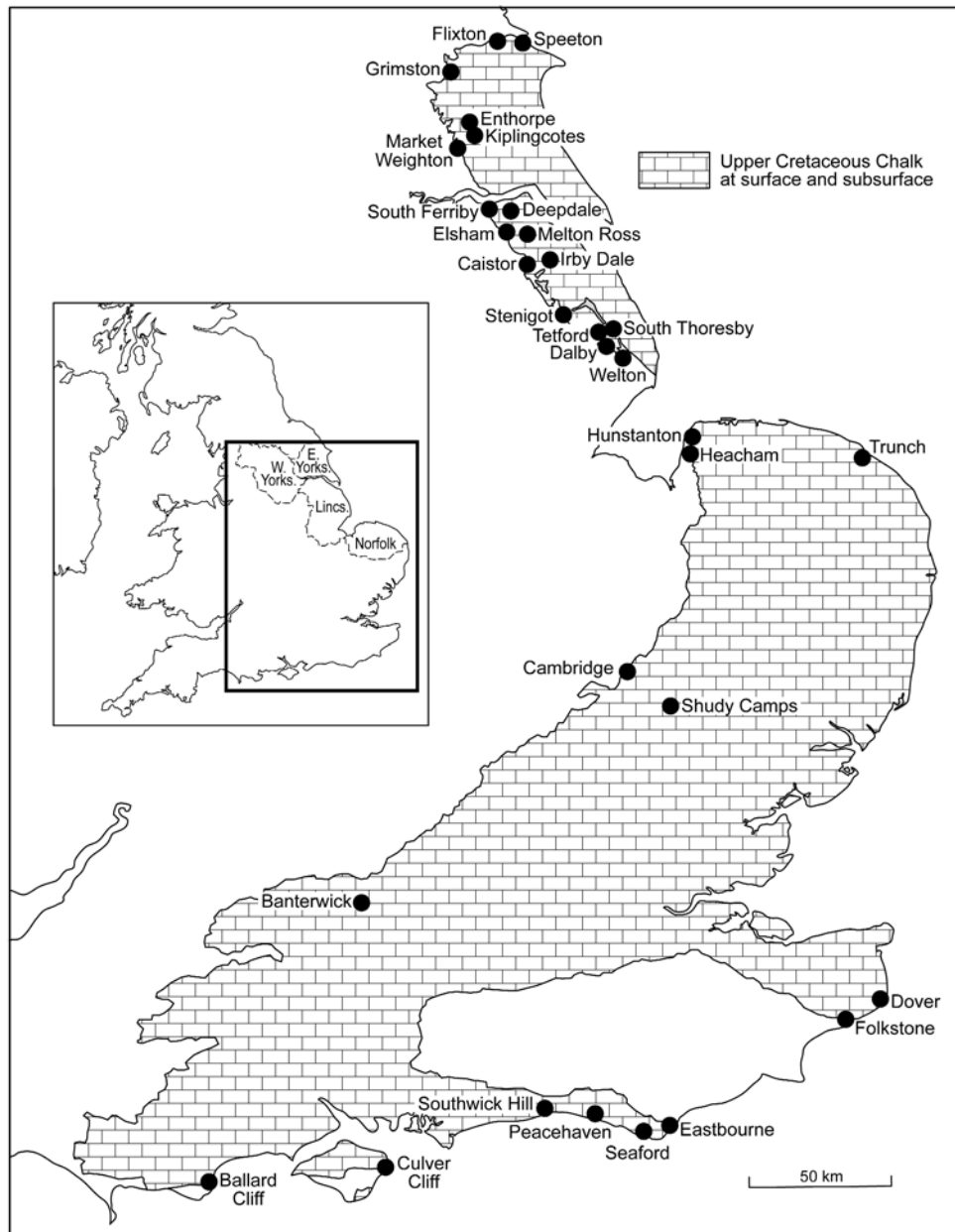
4. *The cerium anomaly recorded by the solid phase should undergo no alteration during diagenesis.* This is of particular importance for the Upper Cretaceous Chalk as it has undergone 60 to 100 million years of diagenesis.

The paper reviews the history and significance of previous research into the rare earth element contents of the Upper Cretaceous Chalk. It describes 120 new rare earth element analyses of the calcite and acetic acid insoluble fractions from chalk samples of Albian, Cenomanian and Turonian age, and then discusses their significance in regard to the extent that their cerium anomalies can be used as palaeoredox proxies of the Chalk Sea and the pore waters of its sediments. A future paper ((Jeans *et al.* in prep.) will describe the application of the cerium anomaly as a paleoredox indicator to the Cenomanian–Turonian Anoxic Event.

## PREVIOUS RESEARCH

Jarvis (1984) was first to investigate the rare earth elements in the Chalk of England. He demonstrated

in a series of white chalks and phosphatic chalks of Santonian–Campanian age that the rare earth elements of the total sample were correlated positively with the  $P_2O_5$  content and were hosted by authigenic carbonate-fluorapatite, the typical apatite of the Chalk, which Jarvis (1980) had separated using 0.5 molar acetic acid buffered at pH5. Jarvis (1984) noted that the shale-normalised rare earth element patterns had pronounced negative cerium anomalies, which were generally similar to the patterns from recent ocean bottom oxic waters; a minor depletion in heavy rare earth elements relative to intermediate ones could reflect an original feature of the Late Cretaceous water mass from which they were derived. The next step in understanding the distribution of the Chalk's rare earth elements were unpublished analyses carried out by CTW at the Natural History Museum (London) in 1987 of total samples and acetic acid insoluble residues from the Lower, Middle and Upper Chalk of England. This demonstrated that the concentration of rare earth elements in the calcite and acid insoluble residues were different. Concentrations in the acid insoluble residues (10–100 ppm) were approximately an order of magnitude greater than in the calcite (1–10 ppm). The general patterns in the two fractions were similar although in detail there were significant differences – of particular interest were variations related to the cerium anomalies. These observations of Jarvis (1980, 1984) and CTW (unpublished) indicate that the rare earth element patterns of the Chalk Sea and its sediment are still preserved in two locations: (1) in the Chalk's authigenic carbonate-fluorapatite that is essentially unaffected by weak acetic acid dissolution and is preserved in the acid insoluble residue, and (2) in the phosphorus-containing calcite that is readily dissolved. Indirect support for this partition of rare earth elements comes from Perrin's (1964) demonstration by the dissolution of a Middle Chalk sample in 2 molar acetic acid buffered at pH3 that a low concentration of phosphorus (147 ppm) resided in the calcite whereas the acid insoluble residue had a much higher concentration (2140 ppm). A possible complication was Perrin's suggestion that some of the phosphorus in the acid insoluble residue resulted from the partial reprecipitation of dissolved phosphate during the experiment; Weir and Catt (1965) found no evidence of this reprecipitation in their separation and study of the clay minerals and their associated apatite from the Upper Chalk of Sussex, however our own experiment (see later) using 2%  $HNO_3$  indicates that reprecipitation of phosphorus may occur.

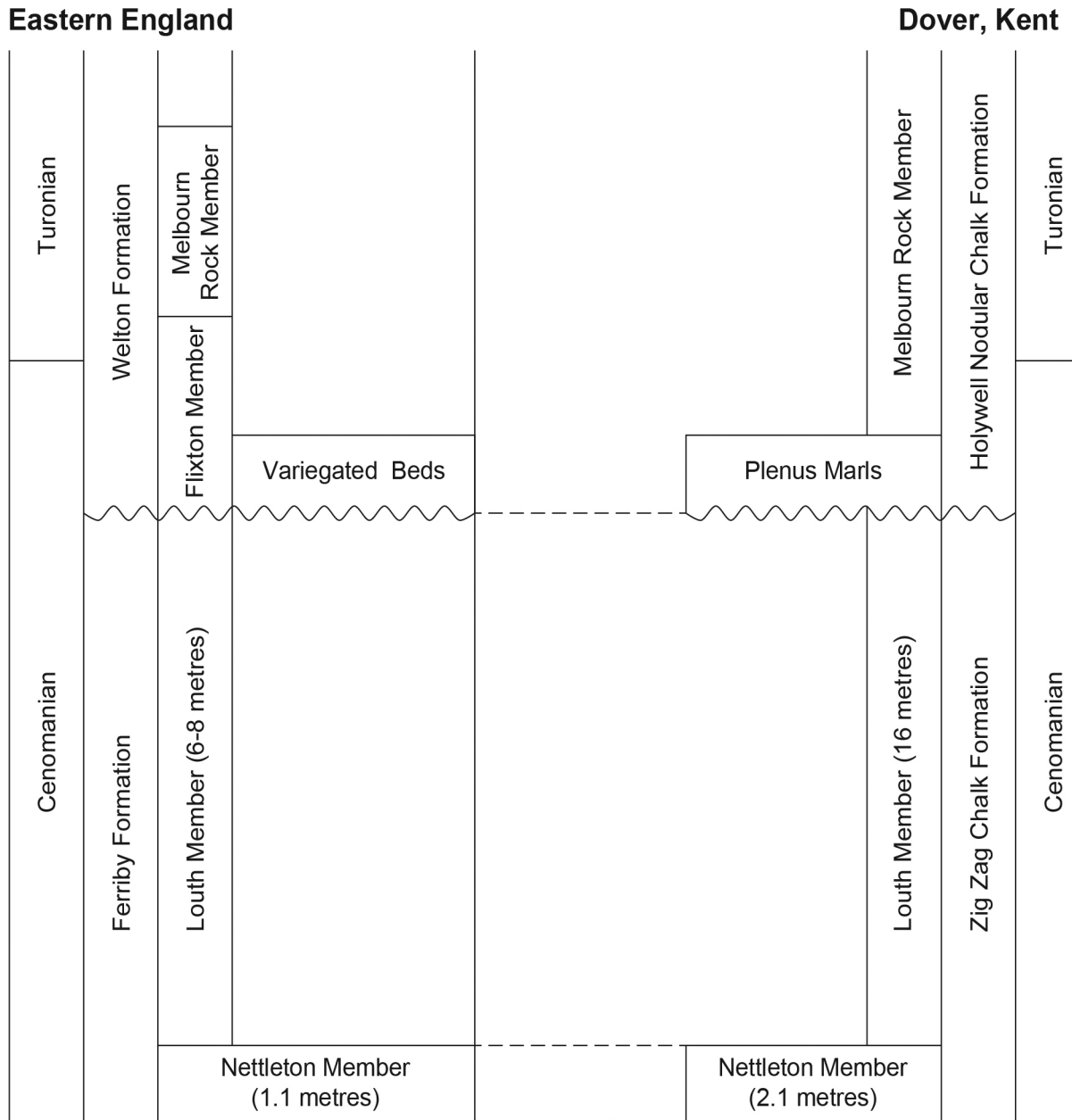


Text-fig. 2. Outcrop and subcrop distribution of the Upper Cretaceous Chalk in England. Locations mentioned in the text are shown as well as those referred to in related papers (Hu *et al.* 2012, 2014; Jeans *et al.* 2012, 2014)

## NEW INVESTIGATION

Our study has been based upon the finding that two cerium anomalies are preserved in the Chalk (see above); one linked to the original calcite skeletons of organisms that lived in the Chalk Sea, the other to carbonate-fluorapatite which reflects conditions in the porewaters of its sediment. The questions we have attempted to answer are as follows: (1) How to differentiate between the anomalies in the original bioclas-

tic calcite and those developed during diagenesis? (2) To what extent has there been fractionation of the rare earth elements between the Chalk Sea and the calcitic skeletons of the organisms that lived in it? (3) Has the cerium anomaly of the pore waters been modified by the addition of volcanic ash as measured by the europium anomaly? And (4) Have the original cerium anomalies in the bioclastic calcite and in the carbonate-fluorapatite in the acetic acid insoluble residues been modified by subsequent diagenesis?



Text-fig. 3. Lithostratigraphical and stratigraphical terms used in eastern and southern England

Text-fig. 2 shows the regional extent of the Upper Cretaceous Chalk in England and the various locations mentioned in the text. Text-fig. 3 shows the stratigraphical terms used.

ANALYTICAL METHOD

120 samples of Chalk have been investigated. The great majority are of Cenomanian age, a small number are of Turonian or Late Albian age. Details of their lo-

cations and stratigraphical levels are given in fig. 10 of Jeans *et al.* (1991) for Flixton, in text-fig. 4 of Hu *et al.* (2012) for Speeton, in text-fig. 5 of Jeans *et al.* (2014) for Elsham, Tetford, South Thoresby and Welton, and in Text-fig. 6 of this paper for Dover and Folkestone.

The new rare earth element analyses (Tables 1–6) are based in part on two methods. The acid insoluble residues (AIR) were extracted by dissolving the calcite fractions of crushed chalk samples in cold 1 molar acetic acid, whereas calcite for analysis was prepared

by dissolving crushed chalk samples (or separated particle size fractions) in 2% nitric acid. Rare earth element analysis was carried out in two phases: prior to 1995 the acid insoluble residues of samples were analysed by CTW using the instrumental neutron activation method (Henderson and Williams 1981); from 1995 onwards the calcite fractions and the acid insoluble residues were analysed by DSW using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). The limit of determination for all rare earth elements was found to be less than 0.1 mg/kg. A determination of expanded uncertainty ( $K=2$ , 95% confidence) derived from eleven measurements of duplicate preparations of a number of reference materials over 5.5 days established uncertainty values of  $\pm 10$ – $12\%$  for the rare earth elements.

The calculation of the cerium and europium anomalies of a particular rare earth element analysis has in this account been based on the following procedures:

$$\text{Ce anomaly} = \frac{\text{Ce s/n}}{(0.8 \times \text{La s/n}) + (0.2 \times \text{Sm s/n})}$$

**Ce s/n**, **La s/n** and **Sm s/n** refers respectively to the shale-normalised values of cerium (Ce), lanthanum (La) and samarium (Sm) for the particular sample relative to the Cody Shale (SCo-1) standard. Cerium anomaly (**Ce\***) values of  $>1.0$ ,  $\sim 1.0$  and  $<1.0$  are referred to, respectively, as positive, neutral (no anomaly) and negative. **Ce\*(calcite)** and **Ce\*(AIR)** refers to the cerium anomalies associated, respectively, with the calcite fractions and acid insoluble residues of the Chalk.

$$\text{Eu anomaly} = \frac{\text{Eu s/n}}{(5.40 \times \text{Sm s/n}) + (4.43 \times \text{Gd s/n})}$$

**Eu s/n**, **Sm s/n** and **Gd s/n** refers respectively to the shale-normalised values of europium (Eu), samarium (Sm) and gadolinium (Gd) for the particular sample relative to the Cody Shale (SCo-1) standard. **Eu\*(calcite)** and **Eu\*(AIR)** refers to the europium anomalies associated, respectively, with the calcite fractions and acid insoluble residues of the Chalk.

#### DIFFERENTIATION BETWEEN CERIUM ANOMALIES

The necessity for ICP-MS analysis of using a weak mineral acid (2% nitric acid) instead of cold 1 molar acetic acid to extract the calcite-associated rare earth elements from our samples could result not only in the dissolution of the calcite but also in the partial dissolution of the carbonate-fluorapatite in which the cerium

anomaly of the Chalk pore waters is preserved. In the most extreme case, all the carbonate-fluorapatite might be dissolved by the 2% nitric acid. The resulting rare earth element pattern would be dominated by, and probably indistinguishable from, that preserved in the carbonate-fluorapatite as the concentration of rare earth elements is an order of magnitude higher than in calcite. Such is not the case because the systematic study of the patterns extracted by these methods from chalks at three locations associated with Cenomanian–Turonian Anoxic Event (Jeans *et al.* in prep.) show that there are two distinct patterns, albeit similar, which may vary independently of each other.

We have also investigated experimentally the effect of using 2% nitric acid by comparing the different values for the cerium anomaly of the calcite obtained from using 0.5 molar acetic acid buffered at pH5 with those obtained by the weak mineral acid. In both instances analysis were carried out by ICP-MS. Eighteen samples were tested, seven from the Plenus Marls at Dover, eleven from the Variegated Beds succession at Flixton. All but one sample displayed an increase in values of the cerium anomaly for the calcite with the 2% nitric acid extract. For the Dover samples (Text-fig. 6) the acetic acid extract values are as follows, the nitric acid extract values are shown in parentheses: **E19**, 0.33(0.35); **E20**, 0.32(0.35); **E21**, 0.35(0.41); **E22**, 0.35(0.40); **E23**, 0.37(0.39); **E24**, 0.34(0.37); **E25**, 0.36(0.41). The Flixton samples (Jeans *et al.*, in prep.) were chosen to represent conspicuous low value spikes of **Ce\*(calcite)** that are clearly differentiated from the **Ce\*(calcite)** values of the underlying and overlying samples. One sample (**LR322**) showed a decrease in value (0.25 cf. 0.27) whereas the remaining samples displayed varying increases. However, the value of only one sample (**Ysa85**) was sufficiently increased to bring it into line with the trend displayed by the underlying and overlying samples. The effects of contact time between 2% nitric acid and a marl sample (**Ysa83**) from Flixton on the cerium anomaly of the calcite was also investigated. The sample was dissolved in excess cold 2% nitric acid over a period of 17 hours with solution samples being extracted first at 5 minutes after the initial contact between acid and sample, then at 10 minute and 20 minute intervals up to 120 minutes, and then at 180, 240, 360 and 1020 minutes. The solutions were analysed for their rare earth elements as well as their phosphorus content (this reflects both phosphorus in the calcite and possibly also in the carbonate-fluorapatite of the acid insoluble residue in which relatively high concentrations of the rare earth elements are hosted; see later). Text-fig. 4 shows the changes with time of the con-



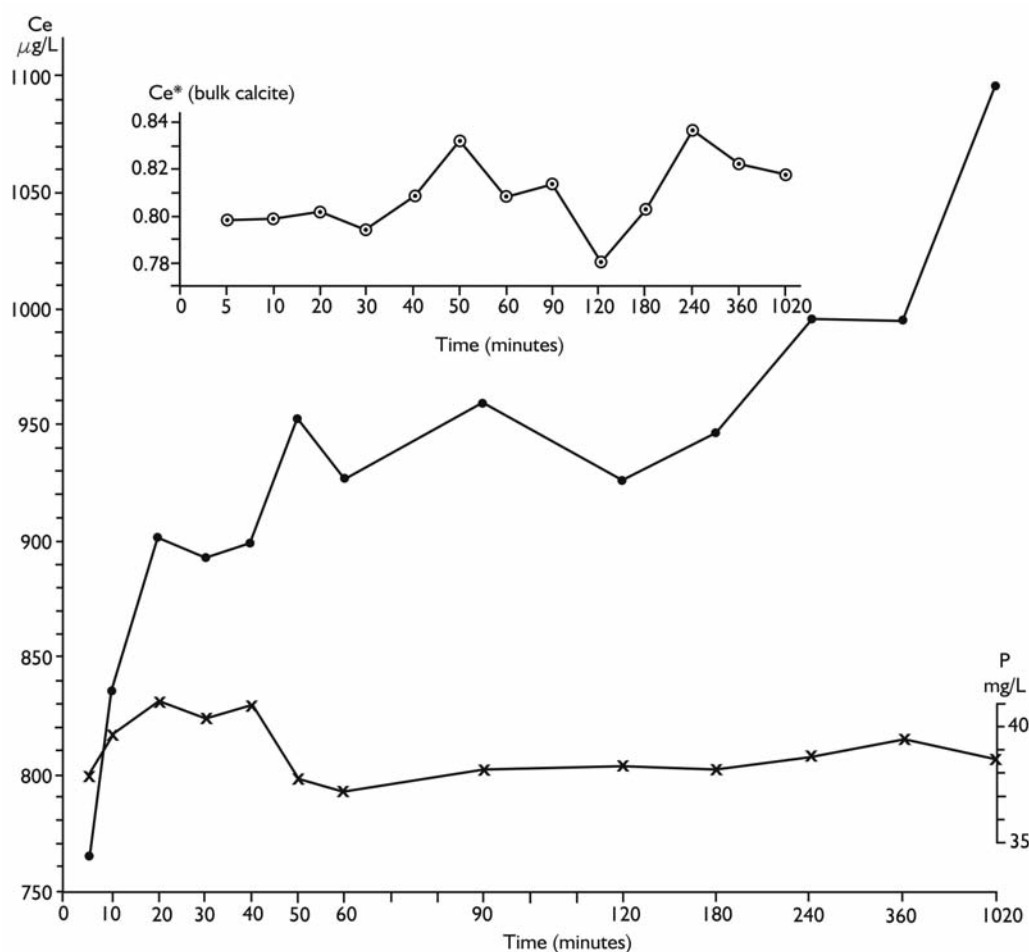
centration of cerium and phosphorus in solution and the corresponding values of the calcite's cerium anomaly. Over the first 2 hour period the average cerium anomaly was 0.81 compared to 0.80 after the first five minutes. In the solution there was no appreciable increase in phosphorus after the first 5 minutes; in contrast, cerium increased from 760  $\mu\text{g/L}$  (5 minutes) to 1100  $\mu\text{g/L}$  (17 hours). A likely explanation is that phosphorus was precipitating out of solution during the experiment (cf. Perrin 1964) and the concentration of 40 mg/L represents the limit for this element under these conditions. As a result of this experiment contact time between sample and 2% nitric acid was limited to 2 hours for the determination of the rare earth elements from the calcite fraction.

Our experiments demonstrate that the use of 2% nitric acid instead of a weak acetic acid digest does make a slight difference by generally increasing the calcite's cerium anomaly; however, if the time of contact between acid and sample is kept to approximately

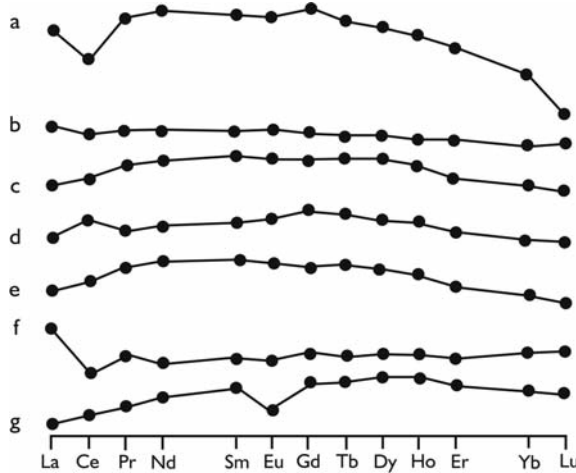
2 hours, there is little change in the pattern of variation, only a displacement to slightly higher values. The conclusion can be drawn that within these limitations the two types of cerium anomalies have been measured, one associated with the calcite fraction, the other with the acid insoluble residue.

#### RARE EARTH ELEMENT PATTERNS IN THE CHALK

A range of typical shale-normalised examples of patterns from the Chalk is illustrated in Text-fig. 5. The great majority of the rare earth element analyses of both the calcite and the acid insoluble residue have shale-normalised patterns with a pronounced negative cerium anomaly, however their shapes are generally different. Calcite patterns display usually a flat form but with enhanced lanthanum values and a gradual increase in the intermediate and heavy groups relative to the light group (Text-fig. 5f).



Text-fig. 4. Cross-plots showing the variations with time in the concentration of cerium (Ce  $\mu\text{g/L}$ ), the cerium anomaly (Ce\* (bulk calcite)) and the phosphorus concentration (P, mg/L) in the solution during the experimental dissolution of the calcite fraction of sample Ysa 83 (Flixton Member, Flixton) in excess cold 2% nitric acid



Text-fig. 5. Rare earth element patterns, normalised to the Cody Shale (SCO-1) standard, of the acetic acid insoluble residues (AIR) and calcite fraction of chalks and marls from Cenomanian and Turonian strata. **a** – Typical, generally convex form with a pronounced negative cerium anomaly (0.60). Sample LR317 (AIR), Melbourn Rock Member, Flixton (Jeans *et al.* 1991, fig. 10). **b** – Flat, less convex form with a negative cerium anomaly (0.88). Sample DoSa4 (AIR), alternating chalk-marl facies, Zig Zag Formation, Ballard Cliff (Text-fig. 13). **c** – Typical convex form with no pronounced cerium anomaly (0.88). Sample LR305 (AIR), Flixton Member, Flixton (Jeans *et al.* 1991, fig. 10). **d** – Typical convex form with a pronounced positive cerium anomaly (1.32). Sample Ysa86 (AIR), Flixton Member, Flixton (Jeans *et al.* 1991, fig. 10). **e** – Typical convex form with no pronounced cerium anomaly (0.99). Sample LR303 (AIR), Flixton Member, Flixton (Jeans *et al.* 1991, Fig. 10). **f** – Typical flat form with a slight gradual increase of heavier REE and a pronounced negative cerium anomaly (0.45). Sample LR303 (calcite), Flixton Member, Flixton (Jeans *et al.* 1991, fig. 10). **g** – Convex form with a slight negative cerium anomaly (0.96) and a pronounced europium anomaly (0.63). Sample J66 (AIR), Deepdale Lower Marl, Welton Formation (Wray and Wood 1998, fig. 3)

Patterns from acid insoluble residues are usually convex in form, displaying a variable, gradual depletion in heavy rare earth elements (Text-fig. 5a). The analyses from the chalk-marl facies of Ballard Cliff (Text-fig. 5b) have a nearly flat pattern, still with a negative cerium anomaly and an inclination to a slight gradual depletion in heavy rare earth elements.

The only exceptional patterns are from strata associated with the Cenomanian–Turonian  $\delta^{13}\text{C}$  excursion at Melton Ross and Flixton, where the cerium anomaly ranges from strongly negative to strongly positive (Text-figs 5a, c, d, e). The exceptional negative cerium anomalies (Text-fig. 5f) are linked to enhanced values of lanthanum. In the majority of samples the value of the cerium anomaly for calcite is less than that for the acid insoluble residue; however, at Melton Ross values may be similar or reversed (Jeans *et al.* in prep.). Compared to published data on the shale-normalised patterns of the rare earth elements from total samples of Santonian–Campanian (Jarvis 1984) and Cenomanian–Turonian strata (Wood *et al.*

1997; Wray and Wood 1988) there is little difference: none of the new analyses displays negative europium anomalies associated with a depletion in light rare earth elements and a slight negative cerium anomaly such as reported by Wray and Wood (1988) from certain marls in eastern England and linked by them to a volcanogenic origin (Text-fig. 5g).

Differences in the concentration of rare earth elements in the calcite and acid insoluble residue (AIR) are usually marked. The La (AIR)/La (calcite) values range from 1.1 to 43 and the averages for different Chalk units range from 3.1 to 43 (Table 1). The Plenium Marls at Dover and the Variegated Beds sequences at Melton Ross and Flixton, both rich in acid-insoluble residue (up to 80–90%), display less marked differences in the concentration of rare earth elements between the acid insoluble residues and calcite fractions than the underlying Louth Member and the overlying Melbourn Rock Member, both of which have a low content of acid insoluble residue (up to 10%). There is, however, no obvious correlation between the weight percent of acid insoluble residue and the La (AIR)/La (calcite) values; the regional variations can be related to the dilution effects of the late diagenetic calcite cementation in eastern England that affected the sections at Melton Ross and Flixton, causing La (AIR)/La (calcite) values often to exceed 15.

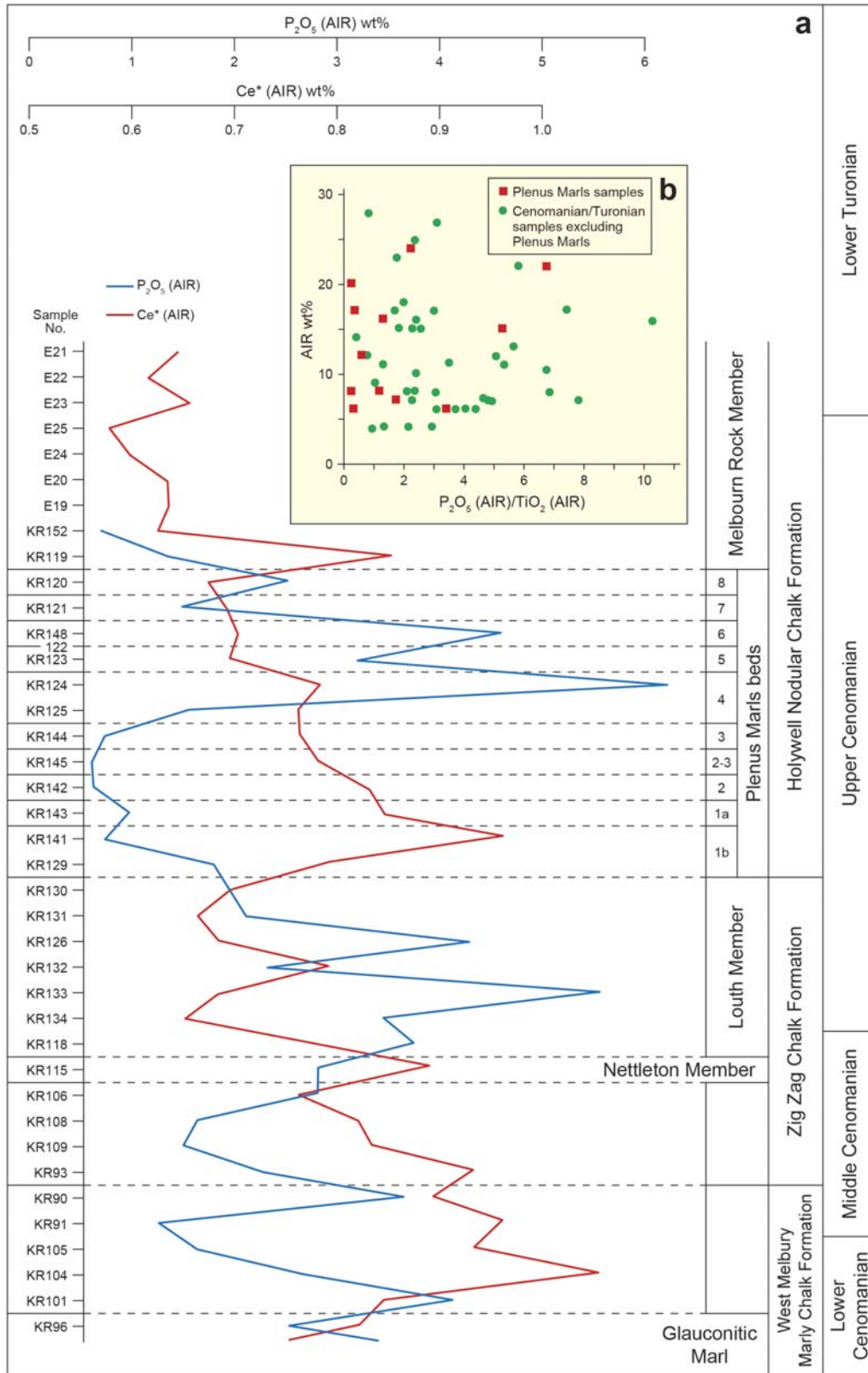
At Dover, in the Cenomanian and Lower Turonian Chalk succession the relationship between the total content of acid insoluble residue, its cerium anomaly and its content of phosphorus (as  $\text{P}_2\text{O}_5$ ) and  $\text{TiO}_2$  has been examined (Text-fig. 6); the rare earth element analyses are in Table 2.  $\text{TiO}_2$  is used as a proxy for the continental silicate detritus in the acid insoluble residue. Text-fig. 6b show that over this stratigraphical interval there is no general correlation. The stratigraphical patterns displayed by the cerium anomaly and the phosphorus are independent of each other (Text-fig. 6a). The conclusion to be drawn is that the cerium anomaly is effectively independent of the continental silicate contribution to the Chalk Sea during Cenomanian and Early Turonian times. Later in this paper it will be shown that when the main part of the acid insoluble residue is volcanic ash this may have a marked influence on its cerium anomaly.

#### FRACTIONATION OF RARE EARTH ELEMENTS BETWEEN THE CHALK SEAWATER AND BIOGENIC CALCITE

The soft uncemented or only very slightly cemented Chalk at Dover can be disaggregated into its



REDOX CONDITIONS IN THE LATE CRETACEOUS CHALK SEA



Text-fig. 6. **a** – This shows (1) The schematic arrangement of samples in the Cenomanian (including the Plenus Marls) and Turonian Chalk at Dover/Folkestone; and (2) the variations in the acid insoluble residue and its  $P_2O_5$  content (reflecting carbonate-fluorapatite) and its cerium anomaly ( $Ce^*(AIR)$ ). **b** – Cross-plot of the acid insoluble residue (AIR) and its  $P_2O_5$  (AIR)/ $TiO_2$  (AIR) ratio for the Cenomanian and Turonian Chalk from Dover/Folkestone shown in Text-fig. 6a

component grains. Text-fig. 7 shows the variation in the cerium anomaly of the fossil skeletal calcite for different particle size fractions in two samples from Dover (Table 2) – KR145 from Jefferies Bed 2-3 of the Plenus Marls, and KR119 from the base of the Melbourn Rock Member. Both samples show high values in the <2 µm fraction (probably coccolith debris-dominated) decreasing in the silt fractions (2–8 µm, 8–63 µm), increasing again in the sand fraction that consists of inoceramid bivalve fragments and other shell fragments, foraminifera and calcispheres. There are two likely explanations: either the various groups of organisms were living under different redox conditions at different levels within the water column and bottom waters; or the grain size-related pattern of cerium anomalies is caused by varying degrees of rare earth element fractionation by different planktonic and benthic organisms such as has been recognised by German and Elderfield (1990) – they observed some evidence that fractionation of rare earth element takes place between seawater and the rare earth elements incorporated into the calcite shells of foraminifera living in modern oceans. Alternative explanations related to diagenetic changes cannot be ruled out, such as (1) the effects of small amounts of diagenetic calcite within foraminifera and calcispheres; (2) selective phosphatisation at different stages of diagenesis introducing new patterns of rare earth elements or modifying old patterns. The cerium anomaly of the calcite from a bulk sample of Chalk will represent the average value from the different calcite components, each of which may represent its own degree of fractionation. However, when the total Chalk sediment is considered, the effects of this fractionation are not apparent. In our study of the lithologically variable Cenomanian–Turonian successions at three locations in England (Jeans *et al.* in prep.) no evidence was found of enhanced Ce\*(calcite) values in the fine-grained coccolith-rich or coarse-

grained inoceramid shell-rich beds as would be expected from our detailed analysis. We draw the conclusion that any effects of differential fractionation between the organisms secreting calcitic skeletons in the Chalk Sea and its seawater have been obscured by much greater changes in the rare earth element chemistry taking place in the Sea itself.

#### VOLCANIC ASH AND THE CERIUM ANOMALY PRESERVED IN THE ACID INSOLUBLE RESIDUES OF MARLS

The europium anomaly is frequently used as a proxy to identify contributions of volcanic ash from evolved magmas in the Chalk of Europe (Wray 1995, 1999; Wray and Wood 1995, 1998, 2002; Wray *et al.* 1995, 1996; Wray and Jeans 2014). Here we use it as a measure of the volcanic contribution to marls in order to investigate its influence on the cerium anomaly. It is based upon the fact that the rare earth element europium can occur in either a di- or trivalent state. Under high temperature reducing conditions such as associated with magma evolution the divalent europium (ionic radius 1.24Å) is readily captured and replaces K (ionic radius 1.33Å) in the crystallisation of potassic feldspar, leaving the magma's rare earth element assemblage impoverished in this element and the assemblage in the feldspar crystals relatively enriched. The degree to which europium is either enriched or impoverished is referred to as the europium anomaly (Eu\*) – see Analytical Methods for calculation. The lanthanum contents are used to reflect the variation in total concentration of rare earth elements. The rare earth element analyses of the acid insoluble residues from one detrital and two volcanogenic marls are in Table 3.

Text-fig. 8 shows the relationships in the acid insoluble residue of a detrital marl from the Turonian

Location	Horizon	Sample Numbers	Range of La (AIR)/La (calcite) values	Average values
Dover	Louth Member	4	8.1 to 13.1	9.8
	Plenus Marls	11	1.8 to 6.7	4.2
	Melbourn Rock Mbr	7	5.5 to 13.5	10
Melton Ross	Louth Member	1	-	12.9
	Flixton Member	26	1.8 to 9.4	3.1
Flixton	Louth Member	1	-	42.8
	Fluxton Member	32	1.2 to 22.8	10.5
	Melbourn Rock Mbr	7	1.1 to 35.6	17
	Welton Chalk	4	1.3 to 31.3	14.2

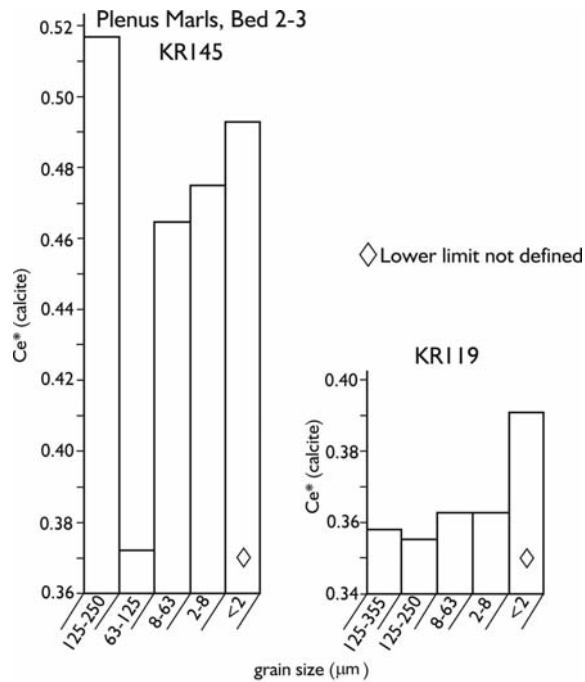
Table 1. Range of La (AIR)/La (calcite) values in various stratigraphical units of the Cenomanian and Turonian Chalk at Dover, Melton Ross and Flixton

## REDOX CONDITIONS IN THE LATE CRETACEOUS CHALK SEA

Sample no.	REE concentrations (ppm) in acid insoluble residues, Dover														Ce*(AIR)
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
KR 90	47.1	75	<i>n.a.</i>	41	7.1	1.6	6.8	0.88	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.34	3.2	0.43	0.84
KR 91	37.4	65	<i>n.a.</i>	33	5.7	1.4	4.8	0.84	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.32	2.9	0.42	0.91
KR 93	40.9	68	<i>n.a.</i>	34	5.9	1.5	5.4	0.79	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.33	3.0	0.46	0.88
KR 96	34.0	50	<i>n.a.</i>	32	5.4	1.3	4.9	0.74	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.29	2.3	0.35	0.77
KR 101	34.3	52	<i>n.a.</i>	30	5.2	1.4	5.3	0.79	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.28	2.4	0.34	0.79
KR 104	32.5	62	<i>n.a.</i>	28	5.2	1.2	5.9	0.8	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.29	3.2	0.42	1.00
KR 105	41.7	71	<i>n.a.</i>	36	7.4	1.6	7.9	0.94	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.33	3.2	0.46	0.88
KR 106	64.5	87	<i>n.a.</i>	54	10.9	2.5	11.1	1.39	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.36	4.4	0.64	0.71
KR 108	61.5	91	<i>n.a.</i>	55	11.5	2.5	12.1	1.51	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.55	4.2	0.51	0.77
KR 109	59.6	89	<i>n.a.</i>	53	10.7	2.5	10.9	1.38	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.54	4.1	0.53	0.78
KR 115	49.0	79	<i>n.a.</i>	43	8.5	1.9	7.6	1.02	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.3	3.2	0.43	0.84
KR 118	58.9	82	<i>n.a.</i>	51	10.4	2.3	11	1.2	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.57	3.5	0.5	0.72
REE concentrations (ppm) in calcite, Dover															
Size fraction	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce*(calcite)
KRI19															
<2 µm	9.70	7.2	1.8	7.5	1.5	0.35	1.6	0.23	1.3	0.25	0.68	0.09	0.51	0.07	0.39
2-8 µm	8.12	5.4	1.3	5.2	1.0	0.24	1.1	0.16	0.97	0.20	0.58	0.08	0.50	0.07	0.36
8-63 µm	9.20	6.1	1.5	5.9	1.1	0.27	1.2	0.19	1.1	0.24	0.68	0.10	0.61	0.09	0.36
125-250 µm	7.40	4.8	1.2	4.7	0.9	0.22	1.0	0.15	0.92	0.20	0.56	0.08	0.49	0.07	0.36
125-355 µm	7.94	5.2	1.2	5.0	1.0	0.23	1.0	0.16	0.98	0.22	0.61	0.09	0.55	0.08	0.36
KRI45															
<2 µm	10.45	9.9	2.0	8.5	1.7	0.38	1.8	0.25	1.4	0.28	0.74	0.10	0.56	0.08	0.49
2-8 µm	8.42	7.4	1.4	57.0	1.1	0.25	1.2	0.18	1.0	0.21	0.61	0.08	0.51	0.07	0.48
8-63 µm	9.19	7.8	1.5	6.0	1.1	0.26	1.3	0.19	1.2	0.25	0.71	0.10	0.60	0.09	0.47
63-125 µm	11.40	11	2.1	8.7	1.7	0.37	1.8	0.27	1.6	0.32	0.90	0.12	0.68	0.10	0.37
125-250µm	14.24	14	2.9	11.9	2.3	0.50	2.5	0.36	2.0	0.41	1.09	0.14	0.76	0.11	0.52

*n.a.* no analysis

Table 2. Rare earth element concentrations and cerium anomalies (Ce\*) in (1) the acid insoluble residues (AIR) of samples from the West Melbury Marly Chalk Formation and the Zig Zag Chalk Formation at Dover and Folkestone; and (2) the calcite of different particle size fractions in samples KR145 and KR119 from, respectively, the Plenus Marls and the Melbourn Member at Dover (Text-fig. 6)



Text-fig. 7. Histograms showing the variation in the cerium anomaly ( $Ce^*(\text{calcite})$ ) within the calcite of the  $<2$   $\mu\text{m}$ , 8–63  $\mu\text{m}$ , 125–250  $\mu\text{m}$  and 125–355  $\mu\text{m}$  particle size fractions from samples KR145 and KR119 of the Plenus Marls and Melbourn Rock Member at Shakespeare Cliff, Dover. Text-fig. 6a for sample horizons

Chalk of Lincolnshire between grain size and (1) the content of phosphorus ( $P_2O_5$ ) and lanthanum, (2) the cerium anomaly, and (3) the europium anomaly.

The same relationships are shown for two volcanogenic marls both of Turonian age, one from the Chalk of Lincolnshire (Text-fig. 9), the other from the Chalk of Söhlde, N.W. Germany (Text-fig. 10). The detrital marl from Lincolnshire displays excellent correlation between the concentration of rare earth elements as represented by lanthanum and the phosphorus ( $P_2O_5$ ) content (Text-fig. 8a). The cerium anomalies are negative and show gradual variations, with the lowest values (0.73, 0.75) in the coarsest and finest particle size fractions and the highest (0.89) in the 2–8  $\mu\text{m}$  size fraction (Text-fig. 8c). Less detailed analysis of the relationship between grain size effects in detrital marls and chalks has been made by measuring the cerium anomalies of total acid insoluble residues as well as the  $<2$   $\mu\text{m}$  fractions from a number of samples (Table 4). This demonstrates that there is no appreciable difference between the bulk acid insoluble residue and its  $<2$   $\mu\text{m}$  fraction. The acid insoluble residues from the volcanogenic marls displayed distinctly different characteristics in their rare earth element patterns. Not only are the patterns

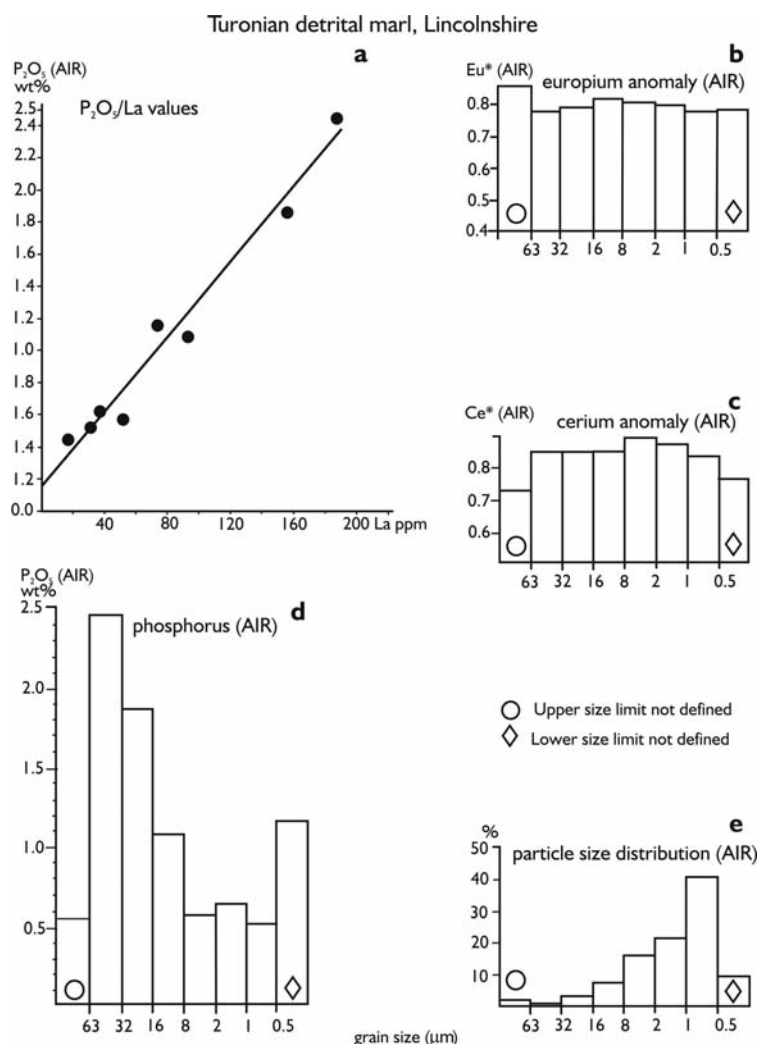
(Text-figs 9b, 10b) of the europium anomalies distinctive, with their relatively high values associated with the sand and coarse silt fractions ( $>32$   $\mu\text{m}$ ) rich in feldspar and the low values in the finer silt and clay fractions ( $<32$   $\mu\text{m}$ ) representing argillised glass shards, whereas in the detrital marl (Text-fig. 8b) there is very little variation in values (0.78 to 0.86). The correlation between  $P_2O_5$  and La is much less obvious (Text-figs 9a, 10a) although there is still a general trend of increasing  $P_2O_5$  with increasing La content. The poor correlation may be due to the presence of minerals of volcanogenic origin with very different rare earth element patterns from those developed in the Chalk. There is considerable variation in the  $P_2O_5$  between the different grain size fractions (Text-figs 9d, 10d). The cerium anomaly values (1.06 to 1.24) are positive in contrast to the negative values of the detrital marl (0.73 to 0.87): this may be related to a combination of (1) an additional supply of phosphorus from the volcanic ash; and (2) argillisation continued into the later and more anoxic stages of diagenesis.

#### EFFECTS OF DIAGENESIS ON THE CHALK'S CERIUM ANOMALIES

Evidence of the role that diagenesis could have played in modifying the rare earth element patterns and cerium anomalies in the Chalk is particularly relevant as it is known to have been affected by a range of diagenetic processes since its deposition that started some 90–100 Ma ago.

#### Cerium anomalies associated with the Chalk's calcite

Jarvis (1980, 2006) has suggested that phosphorus in organic matter reaching the Chalk seafloor was released by microbial action and under certain conditions reached sufficient concentrations to replace (phosphatise) calcium carbonate grains and skeletal matter to form apatite. Thus phosphatisation may have affected the original bioclastic skeletal grains at or just below the Chalk's seawater-sediment interface. A partially phosphatised grain would have a bottom water cerium anomaly as well as the rare earth element pattern of the original carbonate grain or skeleton. Irregular phosphatisation of carbonate grains may be the explanation of some of the variability in the phosphorus contents of the different grain size fractions of the uncemented chalk samples of Late Cenomanian age from Dover (Text-fig. 11). For two of these samples, the variation in cerium



Text-fig. 8. Acid insoluble residue of sample J65 from the detrital Turonian Deepdale Upper Marl, Irby Dale, Lincolnshire (Wray and Wood 1988, fig.3). **a** – Cross-plot of the  $P_2O_5$  (AIR) and Ce\* (AIR) for different particle size fractions. **b** – Eu\*(AIR) values for different particle size fractions. **c** – Ce\*(AIR) values for different particle size fractions. **d** – Variations in  $P_2O_5$  (AIR) in different particle size fractions. **e** – Particle size distribution pattern

anomaly of the calcite in relation to the grain-size fractions is shown in Text-fig. 7.

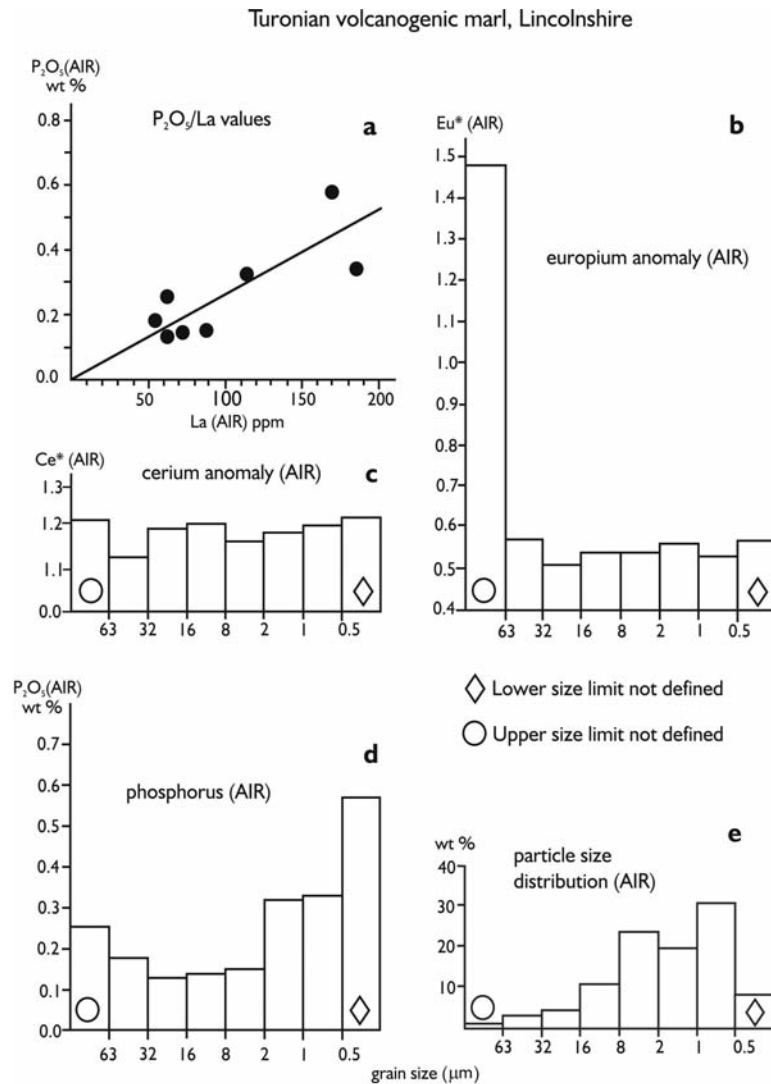
The considerable variation within each sample could be caused either by fractionation by different groups of organisms in secreting their calcite hard parts, or by variations in the cerium anomalies of the seawater in which they lived, or by later phosphatisation, or by some combination of these three processes. Present circumstantial evidence suggests that beneath the water–sediment interface the rare earth elements were not incorporated into the early and late calcite cements but mainly into the very fine-grained apatite crystals that are widespread in the  $<2 \mu m$  clay mineral fractions of the Chalk (Weir and Catt 1965; Jeans 1967, 1968; Perrin 1971).

### Cerium anomalies associated with the Chalk's acid insoluble residues

#### *Nodular chalks and marls*

The early diagenetic development of nodularity in the Chalk sediment by the patchy precipitation of an early Fe-enriched cement (Jeans 1980; Hu *et al.* 2014) has not altered the cerium anomaly of the acid insoluble residues in those parts of the sediment in which it occurred. Table 5 lists the cerium anomalies from the acid insoluble residues of nodules and their matrices (samples F1–10, A1–6) from 15 horizons in the Hunstanton Red Chalk Formation and the Ferriby Chalk Formation at Speeton (Jeans 1980, fig.16 for horizons). There is no systematic





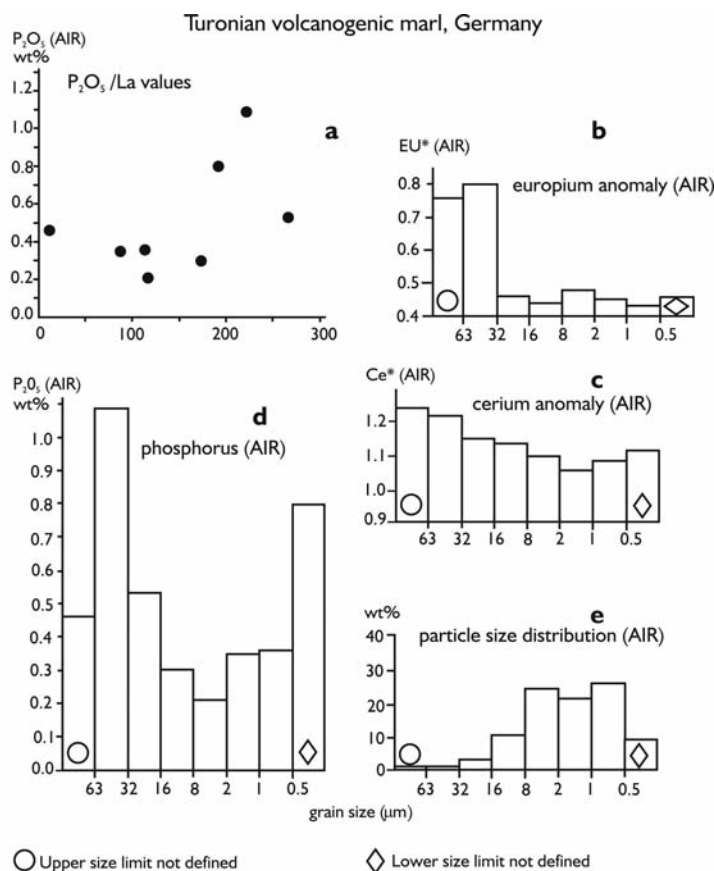
Text-fig. 9. Acid insoluble residue of sample J66 from the volcanogenic Turonian Deepdale Lower Marl, Deepdale, Lincolnshire (Wray and Wood 1988, fig.3). **a** – Cross-plot of  $P_2O_5$  and La for different particle size fractions. **b** –  $Eu^*$ (AIR) values for different particle size fractions: the high value in the  $>63\mu m$  fraction may reflect volcanogenic feldspar. **c** –  $Ce^*$ (AIR) values for different particle size fractions. **d** – Variations in  $P_2O_5$  (AIR) in different particle size fractions. **e** – Particle size distribution pattern

difference in the cerium anomaly between matrix and nodule.

#### *Alternating chalk-marl lithofacies*

This is widespread in the Cenomanian strata of southern England (e.g. Jeans 1968, fig. 4). Many authors (e.g. Gale 1990; Gale *et al.* 1999; Voigt *et al.* 2008) consider the chalk and marl beds as now preserved to represent original differences in lithology, reflecting the effects of Milankovitch cyclicity during the Late Cretaceous. There are problems with this interpretation as the alternating lithofacies can pass laterally, within tens of kilometres, into what appears to be

homogeneous chalk (Jeans 1968, fig. 4). No evidence has yet been put forward to demonstrate that this cyclicity is represented by some other lithological, faunal, or geochemical feature in the homogeneous chalk. Without this evidence such apparent cyclicity could have resulted from a diagenetic unmixing of a homogeneous impure chalk such as has been suggested by Ricken (1987). More recently the general problem of assessing the origin and significance of rhythmic carbonate successions has been reviewed by Westphal and Munnecke (2003) and Westphal *et al.* (2010). Where such alternations are well developed in the Chalk, as in the Zigzag Chalk Formation of mid to late Cenomanian age at Ballard Cliff (Text-fig. 12),



Text-fig. 10. Acid insoluble residue of sample Ge21 from the Turonian volcanogenic marl (Tuff D), Söhlde, N.W. Germany. **a** – Cross-plot of  $P_2O_5$  and La for different particle size fractions. **b** –  $Eu^*$ (AIR) values for different particle size fractions; the high values in the  $>32\mu m$  fraction reflect abundant volcanogenic feldspar. **c** –  $Ce^*$ (AIR) values for different particle size fractions. **d** – Variations in  $P_2O_5$  in different particle size fractions. **e** – Particle size distribution pattern

there is considerable trace element and stable isotope evidence that diagenetic processes have played an important role in the differentiation of the chalk and marl units (Jeans *et al.* 2012, text-fig. 10). Text-fig. 12 shows the relationships between the cerium anomaly of the acetic acid insoluble residue and trace elements (Fe, Mn) of the bulk calcite in this succession of chalk and marl units. The rare earth element data is in Table 3. Typically the marl units have acid insoluble residues with enhanced cerium anomalies and a bulk calcite with lower Fe and Mn content than the chalk units. The enhanced cerium anomalies suggest that the marl units experienced a more anoxic environment in their diagenesis than the chalk units. Other sequences of alternating chalk-marl lithofacies – such as those that make up the Late Cenomanian–Early Turonian Melbourn Rock Member at Eastbourne, Sussex (Jeans *et al.* 2012, text-fig. 11) – are known to display geochemical patterns different from those at Ballard Cliff but which are still related to diagenesis.

**Late diagenetic calcite cementation** is responsible for regional variations in the Chalk's lithification (Jeans *et al.* 2014). It has been investigated in the Louth Member at Dover (unlithified) and at three locations in eastern England (Elsham, Tetford, South Thoresby) where it is lithified. Table 6 shows that there is no variation in the cerium anomaly of the acid insoluble residues corresponding to that in the bulk specific gravity (1.65–2.17), porosity (20–39 vol. %) and calcite cement (0–20 vol. %).

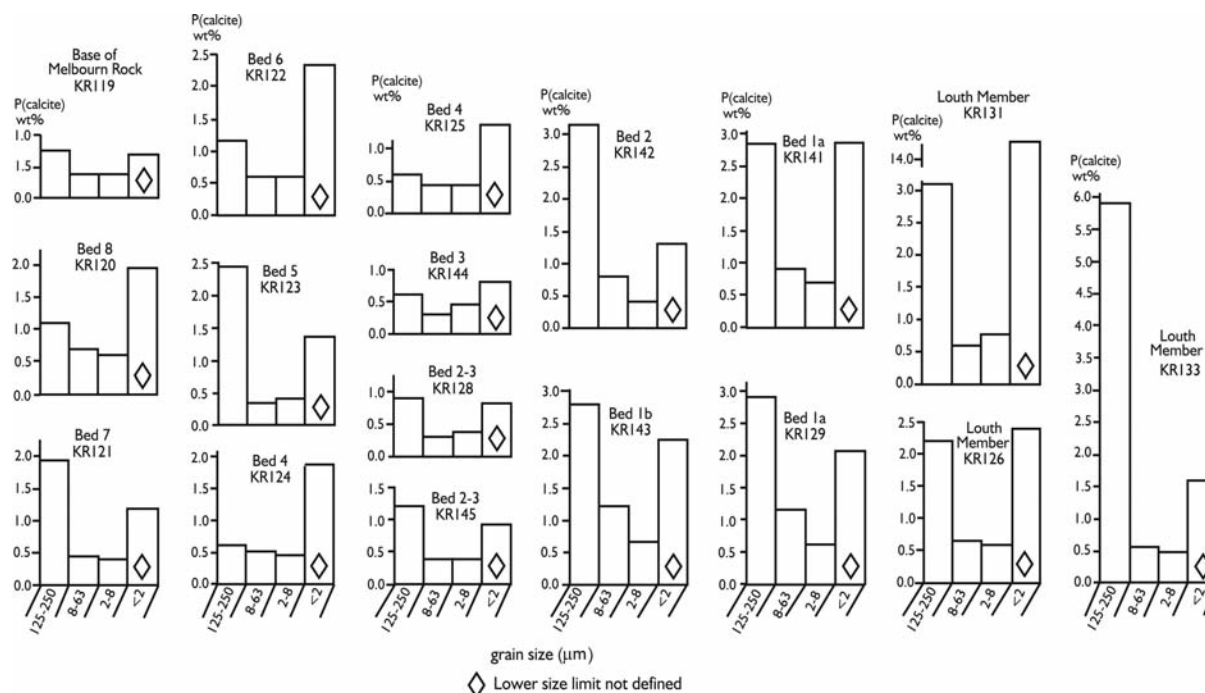
**Late diagenetic sulphidisation** Cross-cutting the Cenomanian and Albian strata in eastern England are sulphidisation zones in which various strata of pink and red chalk and marl have been discoloured with the development of iron sulphides (Text-fig. 13). This is related to a late diagenetic event, some 15 or more million years after the deposition of these strata, linked to tectonic activity along the Flamborough Fault Zone which may be late Cretaceous to early Palaeocene in

Sample no.	REE concentrations (ppm) and cerium and europium anomalies in acid insoluble residues of three Turonian marl bands														Ce*(AR)	Eu*(AIR)
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
GE21 <0.2µm	70	170	20	71	13	1.4	12	1.8	8.4	1.5	3.7	na.	3.0	0.38	1.23	0.46
GE21 0.2-1µm	78	186	22	77	14	1.4	12	1.5	7.7	1.2	3.0	na.	2.4	0.32	1.22	0.43
GE21 1-2µm	50	115	14	49	8.7	0.90	7.5	1.1	5.4	1.0	2.3	na.	2.2	0.29	1.19	0.45
GE21 2-8µm	38	88	11	37	7.1	0.79	6.3	0.85	4.8	0.93	2.3	na.	2.0	0.27	1.17	0.48
GE21 8-16µm	30	72	8.8	31	6.0	0.63	5.6	0.82	4.0	0.78	1.8	na.	1.7	0.19	1.21	0.44
GE21 16-32µm	25	62	7.6	27	5.5	0.59	5.0	0.77	4.2	0.78	1.8	na.	1.7	0.16	1.2	0.46
GE21 32-64µm	24	55	6.9	24	5.2	1.0	5.1	0.85	4.7	0.93	2.4	na.	2.2	0.29	1.13	0.802
GE21 >63µm	25	61	7.3	27	5.0	0.94	5.0	0.72	4.1	0.68	1.8	na.	1.5	0.21	1.22	0.76
J65 <0.2µm	91	146	29	115	22	4.4	23	3.2	18	3.7	9.6	na.	8.7	1.3	0.76	0.79
J65 0.2-1µm	37	62	12	45	9.0	1.7	10	1.5	9.1	2.0	5.8	na.	6.0	0.89	0.81	0.78
J65 1-2µm	41	74	13	51	10	2.1	11	1.7	9.6	2.2	6.3	na.	6.7	1.0	0.85	0.801
J65 2-8µm	57	104	18	69	14	2.7	14	2.0	12	2.6	7.1	na.	7.3	1.0	0.87	0.81
J65 8-16µm	106	185	33	126	24	4.7	23	3.3	18	3.6	9.5	na.	8.2	1.2	0.85	0.82
J65 16-32µm	184	309	57	216	39	7.6	38	5.1	27	5.3	13	na.	10	1.4	0.83	0.79
J65 32-64µm	222	370	68	254	45	8.5	43	5.7	30	5.5	13	na.	9.1	1.2	0.83	0.78
J65 >63µm	22	33	7	25	4.6	1.0	4.7	0.60	3.3	0.61	1.5	na.	1.1	0.16	0.73	0.86
J66 <0.2µm	76	191	26	102	23	3.4	24	4.1	25	5.3	13	na.	12	1.7	1.12	0.57
J66 0.2-1µm	45	113	15	59	15	2.2	18	3.3	21	4.3	12	na.	11	1.6	1.09	0.53
J66 1-2µm	37	87	12	44	11	1.7	13	2.5	16	3.3	8.9	na.	8.7	1.2	1.06	0.56
J66 2-8µm	48	116	16	60	14	2.0	15	2.9	18	3.6	9.6	na.	8.8	1.2	1.1	0.54
J66 8-16µm	70	173	24	91	19	2.6	20	3.3	20	4.0	10	na.	8.7	1.3	1.14	0.54
J66 16-32µm	104	266	39	153	31	3.9	30	4.4	24	4.6	12	na.	9.3	1.3	1.15	0.51
J66 32-64µm	79	220	33	129	26	3.3	22	3.1	16	2.8	7.0	na.	5.0	0.71	1.22	0.57
J66 >63µm	3.6	10	1.2	5.3	1.1	0.40	1.1	0.15	0.84	0.15	0.43	na.	0.38	0.07	1.24	1.48
Sample no.	REE concentrations (ppm) and cerium anomalies of acid insoluble residues from the alternating chalk-marl facies, Ballard Cliff Dorset														Ce*(AR)	
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
DoSa1	41	65	9.1	36	7.1	1.6	6.0	0.90	5.1	1.0	2.9	na.	2.2	0.33	0.82	
DoSa2	42	71	9.6	38	7.5	1.7	6.2	0.94	5.3	1.1	3.2	na.	2.5	0.36	0.86	
DoSa3	40	65	9.5	38	7.6	1.7	6.4	0.94	5.1	1.0	2.8	na.	2.1	0.32	0.82	
DoSa4	34	57	7.5	28	5.6	1.3	4.6	0.69	4.0	0.79	2.4	na.	2.0	0.30	0.88	
DoSa5	38	59	8.5	34	6.5	1.5	5.7	0.84	4.7	1.0	2.8	na.	2.1	0.30	0.8	
DoSa6	43	70	9.9	41	8.1	1.9	6.8	0.1	5.7	1.1	3.2	na.	2.4	0.35	0.84	
DoSa7	36	59	8.3	33	6.4	1.5	5.4	0.8	4.5	0.9	2.6	na.	2.1	0.30	0.83	
DoSa8	47	74	11	45	8.9	2.0	7.6	1.15	6.5	1.3	3.6	na.	2.6	0.39	0.79	
DoSa9	44	69	10	41	8.2	2.0	7.2	1.07	6.1	1.2	3.5	na.	2.6	0.37	0.78	
DoSa10	38	62	8.8	34	6.7	1.6	5.6	0.87	5.0	1.0	3.0	na.	2.4	0.34	0.84	
DoSa11	41	63	9.3	37	7.2	1.7	6.1	0.94	5.3	1.1	3.1	na.	2.4	0.34	0.8	
DoSa12	36	60	8.1	32	6.2	1.4	5.3	0.80	4.5	0.91	2.7	na.	2.1	0.31	0.86	
DoSa13	36	60	8.4	33	6.6	1.5	5.3	0.79	4.5	0.88	2.7	na.	2.1	0.32	0.84	
DoSa14	37	62	8.6	33	6.3	1.5	5.4	0.82	4.5	0.93	2.7	na.	2.1	0.33	0.85	
DoSa15	39	64	9.1	36	7.1	1.6	5.9	0.91	5.0	1.1	3.1	na.	2.5	0.37	0.83	
DoSa16	43	72	10	41	8.3	1.9	6.6	1.05	5.7	1.2	3.5	na.	2.8	0.40	0.84	
DoSa17	40	65	9.4	39	7.6	1.8	6.0	0.97	5.3	1.1	3.2	na.	2.5	0.37	0.81	

n.a. no analysis

Table 3. Rare earth element concentrations and the cerium (Ce\*) and europium (Eu\*) anomalies in the acid insoluble residue (AIR) of (1) detrital and volcanogenic marl bands of Turonian age from Germany and Lincolnshire; and (2) samples from a sequence of chalk-marl alternations in the Cenomanian Zig Zag Chalk Formation at Ballard Cliff, Dorset (Text-fig. 13)

## REDOX CONDITIONS IN THE LATE CRETACEOUS CHALK SEA



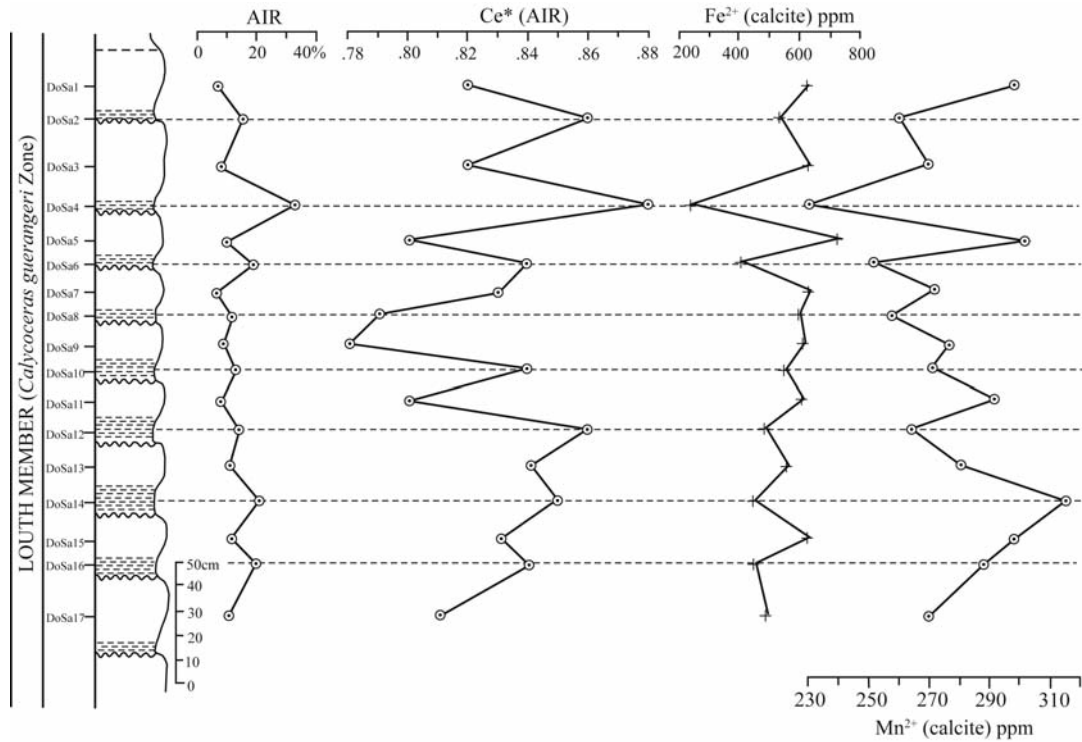
Text-fig. 11. Histograms showing the variation in phosphorus (P) within the bulk calcite of the <2 µm, 2–8 µm, 8–63 µm and 125–250 µm particle size fractions from various samples of the Plenius Marls and adjacent sediments at Shakespeare Cliff, Dover (Text-fig. 6a for sample horizons). KR131 is the only sample with a <2 µm fraction which has a phosphorus content (14 wt %) in excess of the maximum value (~2.5 wt %) recorded by Siesser (1977) for the skeletal calcite of recent and Tertiary Coccolithophoridae

age (Starmer 1995, 2008, 2013; Jeans *et al.* 2014). This allowed solutions rich in sulphate (or H<sub>2</sub>S) and hydrocarbons to invade these strata along faults and joints causing widespread anoxia and sulphidisation of the precursor of the hematite colouring pigment. Table 6 shows that the cerium anomalies of the acid insoluble residues at Elsham from within the sulphidisation zone of the Louth Member average 0.57 whereas out-

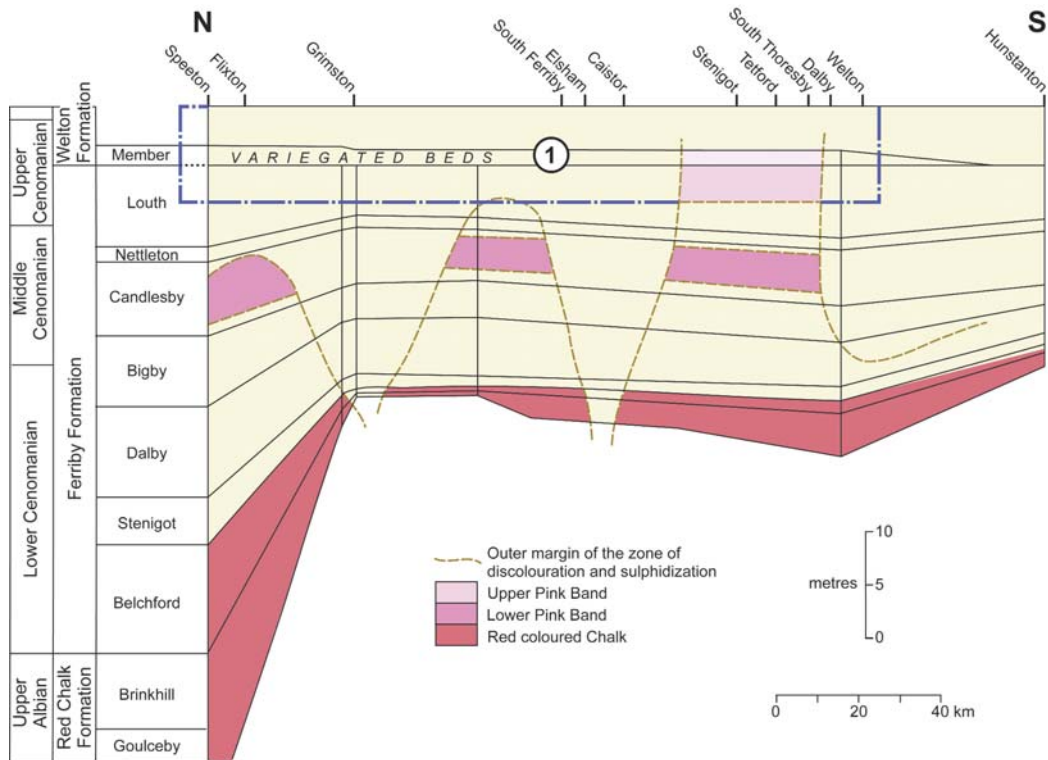
side the zone at Tetford and South Thoresby the values average 0.56. There is thus no appreciable difference in the cerium anomalies of the acid insoluble residues from within and outside the sulphidisation zone albeit the number of analyses is small. The sulphidisation is likely to have occurred under anoxic conditions, when the pore waters would have had a positive or neutral cerium anomaly. The most likely explanation is that

Sample	Location/horizon	Ce*(AIR)	
		Total	< 2µm
LR320	Flixton, Welton Formation	1.17	1.1 1
LR312	Flixton, Melbourn Rock, Welton Formation	0.82	0.8 5
LR309	Flixton, Flixton Member, Welton Formation	0.54	0.8 3
LR302	Flixton, Variegated Beds, Welton Formation	1.18	1.1 1
Ysa85	Flixton, Variegated Beds, Welton Formation	1.1	1.2
!+(56, 57)	Speeton, 2.96m below base of Nettleton Member, Ferriby Fm	0.81	0.8 5
LR368	Tetford Hill, Flixton Member, Ferriby Fm	0.57	0.5 9
LR382	Welton, Louth Member, Ferriby Fm	0.51	0.5 1
KR141	Dover, Bed 1a, Plenius Marls	0.93	0.9 3

Table 4. Ce (AIR) anomalies of the total AIR and the <2µm AIR fraction of chalks from eastern and southern England



Text-fig. 12. Sequence of chalk-marl alternations in the Louth Member (Zig Zag Formation, Ballard Cliff, Dorset) showing the generally similar variations of the acid insoluble residue (AIR) and its cerium anomaly (Ce\*(AIR)) in contrast to the pattern of Fe<sup>2+</sup>(calcite) and Mn<sup>2+</sup>(calcite) variation in the bulk calcite



Text-fig. 13. Horizontal section through the Red Chalk, Ferriby and basal Welton formations in eastern England based on Bower and Farmery (1910), Wood and Smith (1978) and Jeans (1980). The extent of the main bands of red and pink chalk and the zone of discolouration are shown. Zone 1 indicates the stratigraphical and regional extent of a detailed geochemical investigation undertaken on the cementation of the Chalk by Jeans *et al.* (2014). The cross-cutting zones of discolouration are caused by sulphidisation as the result of allochthonous solutions rich in sulphate (or H<sub>2</sub>S) and hydrocarbons penetrating the Chalk along active tectonic zones perhaps some 15 Ma or more years after their deposition



## REDOX CONDITIONS IN THE LATE CRETACEOUS CHALK SEA

REE concentrations (ppm) in acid insoluble residues from Speeton, Elsham, Tetford, South Thoresby, and Welton																
Speeton, AIR	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce*(AIR)	
F1 matrix	90	151	26	107	23	5.5	19	2.81	15	2.8	7.5	<i>n.a.</i>	5.3	0.78	0.79	
F1 nodule	157	292	40	170	37	8.6	32	4.73	26	5.1	13.4	<i>n.a.</i>	8.6	1.22	0.9	
F2 matrix	93	204	26	107	23	5.3	18	2.81	15	2.8	7.7	<i>n.a.</i>	5.7	0.81	1.04	
F2 nodule	126	296	36	150	34	8.0	28	4.15	22	4.2	11	<i>n.a.</i>	7.5	1.05	1.09	
F3 matrix	56	111	16	65	14	3.2	11	1.58	8.2	1.5	4.0	<i>n.a.</i>	2.7	0.35	0.93	
F3 nodule	52	103	15	61	14	3.2	11	1.56	8.1	1.5	3.8	<i>n.a.</i>	2.3	0.31	0.93	
F4 matrix	74	146	21	87	19	4.4	14	2.16	11	2.0	5.5	<i>n.a.</i>	3.8	0.54	0.93	
F4 nodule	55	107	15	60	12	2.9	10	1.48	7.4	1.3	3.5	<i>n.a.</i>	2.4	0.31	0.94	
F5 matrix	59	126	16	66	14	3.1	11	1.6	8.7	1.6	4.3	<i>n.a.</i>	3.2	0.44	1.03	
F5 nodule	72	170	20	85	19	4.1	15	2.2	11	2.1	5.7	<i>n.a.</i>	3.5	0.50	1.1	
F6 matrix	44	78	13	53	11	2.6	8.9	1.3	6.4	1.2	3.2	<i>n.a.</i>	2.1	0.27	0.83	
F6 nodule	61	107	18	80	18	4.3	14	2.1	11	2.0	5.3	<i>n.a.</i>	3.1	0.41	0.79	
F7 matrix	62	119	19	80	18	4.2	14	2.16	11	2.1	5.7	<i>n.a.</i>	3.9	0.53	0.88	
F7 nodule	61	107	17	76	17	4.0	14	2.1	11	2.1	5.3	<i>n.a.</i>	3.5	0.45	0.81	
F8 matrix	51	95	15	65	14	3.3	11	1.6	8	1.6	4.3	<i>n.a.</i>	2.9	0.42	0.86	
F8 nodule	28	50	8	32	7	1.6	5.5	0.8	4.4	0.8	2.3	<i>n.a.</i>	1.6	0.22	0.85	
F9 matrix	79	130	23	94	20	4.0	17	2.5	14	2.6	6.9	<i>n.a.</i>	4.4	0.62	0.77	
F9 nodule	67	110	18	78	17	4.2	14	2.2	12	2.3	5.8	<i>n.a.</i>	3.7	0.52	0.78	
F10 matrix	46	75	12	47	9	2.2	7.6	1.2	6.6	1.3	3.7	<i>n.a.</i>	2.8	0.38	0.81	
F10 nodule	64	108	18	78	14	4.2	14	2.2	12	2.3	5.8	<i>n.a.</i>	3.9	0.55	0.77	
A1 matrix	57	92	17	74	16	3.9	14	1.9	9.8	1.8	5.0	<i>n.a.</i>	2.8	0.38	0.79	
A1 nodule	59	100	17	74	16	3.9	13	2.0	10	1.8	5.2	<i>n.a.</i>	3.2	0.45	0.73	
A2 matrix	70	107	19	78	17	4.0	14	2.1	11	2.2	6.4	<i>n.a.</i>	3.8	0.52	0.73	
A2 nodule	64	100	17	72	16	4.0	14	2.0	11	2.1	5.9	<i>n.a.</i>	3.4	0.48	0.95	
A4 matrix	75	124	19	91	20	4.8	17	2.5	14	2.5	7.5	<i>n.a.</i>	4.5	0.62	0.77	
A4 nodule	72	119	19	83	17	4.2	16	2.3	12	2.4	6.7	<i>n.a.</i>	3.8	0.55	0.79	
A5 matrix	65	105	19	83	19	4.3	15	2.2	11	2.1	6.2	<i>n.a.</i>	3.9	0.55	0.74	
A5 nodule	60	106	16	67	15	3.6	13	1.8	9.4	1.8	5.2	<i>n.a.</i>	3.0	0.41	0.84	
A6 matrix	84	114	23	100	22	5.2	18	2.6	12	2.5	7.2	<i>n.a.</i>	4.1	0.58	0.64	
A6 nodule	75	96	19	81	17	4.2	15	2.2	12	2.2	6.3	<i>n.a.</i>	3.6	0.49	0.61	
1+(56),1+(57)	45	77	13	54	11	2.6	10	1.6	8.1	1.5	3.5	<i>n.a.</i>	2.6	0.38	0.81	
1+(56),1+(57)<2µm	49	89	15	63	13	3.1	12	1.9	9.5	1.9	4.2	<i>n.a.</i>	3.0	0.41	0.85	
Elsham, AIR	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce*(AIR)	
LR 337a	77	97	21	85	17	4.1	17	2.19	12	2.5	5.8	0.68	3.6	0.53	0.62	
LR 338a	80	94	20	83	16	4.0	17	2.24	12	2.6	6.0	0.72	3.9	0.54	0.6	
LR 339a	102	115	28	116	23	5.6	24	3.11	17	3.6	7.9	0.89	4.7	0.64	0.55	
LR 340	104	117	27	112	22	5.4	23	3.06	16	3.6	8.0	0.93	4.9	0.69	0.55	
LR 341	89	96	23	99	19	4.8	21	2.67	14	3.1	6.8	0.77	3.8	0.51	0.53	
LR 342	105	128	28	117	23	5.6	24	3.15	17	3.6	7.9	0.86	4.3	0.57	0.59	
Tetford, AIR	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce*(AIR)	
LR 368	86	100	<i>n.a.</i>	92	19	4.4	17	2.17	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	4.6	<i>n.a.</i>	0.57	
LR 368<2µm	62	80	20	81	16	3.9	16	2.35	12	2.4	5.6	<i>n.a.</i>	3.4	0.44	0.59	
LR 376	70	80	20	81	16	3.9	16	2.51	12	2.5	5.7	<i>n.a.</i>	1.3	0.45	0.55	
LR 378	91	95	24	98	19	4.7	20	3.18	15	3.2	7.7	<i>n.a.</i>	4.7	0.63	0.52	
LR 379	70	79	20	81	16	3.9	16	2.44	12	2.5	5.4	<i>n.a.</i>	3.5	0.49	0.55	
LR 380	75	87	20	84	17	3.9	16	2.56	13	2.7	6.4	<i>n.a.</i>	4.2	0.61	0.57	
LR 381	32	38	7.8	29	5.3	1.3	4.9	0.82	4.2	0.9	2.2	<i>n.a.</i>	1.7	0.23	0.62	
South Thoresby, AIR	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce*(AIR)	
LR 354	95	112	26	108	21	5.3	22	2.92	15	3.3	7.3	0.82	4.1	0.52	0.57	
Lsn 24	105	124	30	126	26	6.0	25	3.25	17	3.6	8.0	0.88	4.5	0.62	0.56	
LR 355	100	115	28	116	24	5.6	23	3.10	17	3.5	7.5	0.84	4.3	0.57	0.55	
LR 356	101	114	26	108	22	5.3	22	2.94	16	3.4	7.5	0.83	4.5	0.58	0.56	
LR 357	115	124	31	127	25	6.2	26	3.55	19	4.2	9.4	0.92	5.8	0.79	0.53	
LR 358	90	110	25	102	21	5.0	21	2.85	16	3.4	7.8	0.99	5.1	0.70	0.59	
Welton, AIR	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ce*(AIR)	
LR 382	83	85	22	89	17	4.1	17	2.63	13	2.6	6.3	<i>n.a.</i>	3.9	0.51	0.51	
LR 382<2µm	82	87	23	94	19	4.6	20	2.86	14	2.9	6.6	<i>n.a.</i>	4.0	0.53	0.51	

*n.a.*, no analysis

Table 5. Rare earth element concentrations and the cerium anomaly (Ce\*) in the acid insoluble residues (AIR) of (1) nodular chalks and nodular marls from the Ferraby Formation and the Hunstanton Red Chalk Formation of Speeton (Hu *et al.* 2012, text-fig.4), and (2) lithified chalk from the Louth Member of the Ferraby Formation at Elsham, Tetford, South Thoresby and Welton (Jeans *et al.* 2014, text-fig. 5)

Sulphidised red facies. Elsham		Red facies. Tetford Hill		Red facies. South Thoresby		Non-red facies. Dover	
Sample	Ce*(AIR)	Sample	Ce*(AIR)	Sample	Ce*(AIR)	Sample	Ce*(AIR)
LR 342	0.59	LR 376	0.55	LR 354	0.57	KR129	0.62
LR 341	0.53	LR 378	0.52	Ls a24	0.56	KR131	0.51
LR 340	0.55	LR 379	0.55	LR 355	0.55	KR126	0.53
LR 339a	0.55	LR 380	0.57	LR 356	0.56	KR132	0.62
LR 338a	0.6	LR 381	0.62	LR 357	0.53	KR118	0.6
LR 337a	0.62			LR 358	0.59		
<b>Average Ce*(AIR)</b>	<u>0.57</u>		<u>0.56</u>		<u>0.56</u>		<u>0.58</u>
<b>Av. bulk specific gravity</b>	2.12		2.12		2.17		1.65
<b>Av. porosity</b>	21.5%		21.5%		19.6%		39.3%
<b>Estimated volume of Fe-rich cement</b>	17.8%		17.8%		19.6%		0.0 %

Table 6. Ce (AIR) anomalies, bulk specific gravity, porosity and cement volume in three diagenetic facies of the Louth Member, eastern and southern England.. The sulphidised red facies of Elsham represent chalk that originally contained red hematite pigment that has been lost during late-stage non-intrinsic diagenesis as the result of invasive pore fluids rich in sulphate (or H<sub>2</sub>S) and hydrocarbons (see Text-fig. 9 and Jeans *et al.* 2014). The red facies at Tetford Hill and South Thoresby are examples of the Upper Pink Band where it is preserved. The non-red facies of the Louth Member at Dover has never contained a hematite pigment during its diagenetic history

carbonate-fluorapatite, the preferred host to the rare earth elements, was either no longer being precipitated or, if it was, it was in such minor amounts that its content of rare earth elements did not modify the overall pattern of the acid insoluble residue.

## CONCLUSIONS

Our investigation of the cerium anomalies in the Upper Cretaceous Chalk of England suggests the following:

1. Two population of rare earth elements are preserved, one in the calcite fraction, the other in the carbonate-fluorapatite of the acetic acid insoluble residue.
2. The two rare earth element populations can be differentiated analytically by either selective acid dissolution using cold 1 molar acetic acid or by timed selective acid dissolution using cold 2% nitric acid.
3. The cerium anomaly associated with the pattern of rare earth elements in the Chalk's calcite is an indicator of the general palaeoredox conditions in the Chalk Sea although there is evidence that there may have been some fractionation in the formation of the calcite shells of the fossil organisms that make up the Chalk.
4. The cerium anomaly linked to the pattern of rare earth elements associated with the carbonate-fluorapatite of the acetic acid insoluble residue is a measure of the average palaeoredox conditions in the porewaters of the Chalk sediment during the phase of diagenesis when the host apatite mineral

was being precipitated. Later stages of diagenesis are not recorded.

5. Diagenesis has had no apparent effect on the cerium anomalies of either the calcite fraction or the acetic acid insoluble residue.
6. Contributions of volcanic ash may modify the cerium anomaly of the acetic acid insoluble residue by the addition of phosphorus, thus allowing the precipitation of carbonate-fluorapatite to extend into conditions of greater anoxia.

A later paper (Jeans *et al.* in preparation) will demonstrate how the application of the cerium anomaly method in combination with other geochemical proxies to three sections (Flixton, Melton Ross, Dover) in the Chalk of England spanning the Cenomanian–Turonian Anoxic Event provides a new insight into the oceanographic conditions linked to this ocean-wide event and its associated faunal changes.

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