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Geochemical constraints on the origin of enigmatic cemented chalks, Norfolk, UK

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Abstract – Very hard cemented chalk stacks and crusts found locally in the upper part of the Cretaceous Chalk of north Norfolk, UK, are related to solution features. The solution features, mainly pipes and caves, formed after deposition of the overlying Middle Pleistocene Wroxham Crag, probably by routing of sub-glacial, or glacial, melt-waters derived from late Pleistocene glaciers. New geochemical (particularly stable isotope) data shows that cementation of the chalks, although related spatially to the solution features, was not caused by glacier-derived waters. The carbon isotope composition of the chalk cements is typically around −9.5 ‰, indicative of biologically active soils. Moreover, the oxygen isotope compositions of the cements, around −5 ‰, are incompatible with water $\delta^{18}O$ values much below −9 to −10 ‰ (which probably precludes isotopically negative glacier-derived water), as resulting palaeo-temperatures are below zero. Taken together, the isotope data suggest chalk cementation occurred under interglacial conditions similar to the present. Dissolved calcium carbonate for cementation came from dissolution of reworked chalk in overlying MIS 12 glacial tills.

Keywords: chalk, cemented chalk, calcite, palaeotemperature, stable isotopes, trace elements.

1. Introduction

There is much current research interest in near-earth-surface terrestrial carbonate sediments (e.g. speleothems) as indicators of palaeoenvironmental and palaeoclimatic conditions, particularly in the Quaternary. Speleothems are now considered high-quality archives of palaeoclimatic data (McDermott, 2004); tufas, calcretes and terrestrial stromatolitic crusts also contain valuable palaeoenvironmental information (e.g. see Cerling, 1984; Andrews, 2006), typically through their stable isotope compositions.

This study focuses on a new aspect of these types of deposits, namely groundwater calcite cementation of pre-existing carbonate rocks related to karstic solution structures. We describe here masses of very hard cemented Cretaceous chalks forming stacks and crusts on the coast in north Norfolk, England (Burnaby, 1950). The upper parts of the stacks have a distinctive conical-tubular, vase-like structure, which has been related to the shape of solution pipes in the Chalk (Burnaby, 1950). While there is little doubt that these hardened chalks are related to solution features in the chalk, it is not clear when or how they formed. Burnaby (1950) thought the solution and cementation of these chalks occurred sub-aerially before deposition of overlying sediments. He attributed the cementation to sub-aerial dissolution and reprecipitation reactions on the chalk surface driven by the decomposition of organic matter. In contrast, Thurston & Whittlesea (2002) attributed stack formation to preferential cementation of sub-glacial sinkholes during the last glaciation. Given the disparity between these interpretations, we have re-examined the hardened chalks with a variety of modern petrographic and geochemical techniques to try to clarify when and how the cementation occurred. We were particularly curious to establish whether stable isotope geochemistry could prove or disprove the involvement of glacial melt water in this example of chalk cementation.

2. Localities and stratigraphy

This study is based on exposures from the coastal cliff section almost midway between Sheringham and Weybourne Hope in Norfolk, England (Fig. 1). The sampled stacks and crusts are at the west end [NGR TG 12733 43536] of the sites described by Burnaby (1950). Exposures were much more extensive in the late 1940s when Burnaby made his field observations, and the more easterly sites near Sheringham and West Runton have been mostly removed by marine erosion.

The cliffs in this area comprise three lithostratigraphic units (Fig. 2). The Weybourne Chalk Member (Johansen & Surlyk, 1990) crops out at the cliff base, dipping gently E to expose about 30 m of strata along the studied section (Peake & Hancock, 1961, 1970). The upper surface of the chalk is locally highly corroded by solution pipes and small caves. Although Burnaby (1950) and Peake (quoted in Pitchford, 1991) thought the karstification occurred before Wroxham Crag deposition (see below), it is actually quite clear that crag sediments have been lowered and deformed into solution pipes post-depositionally: karstification

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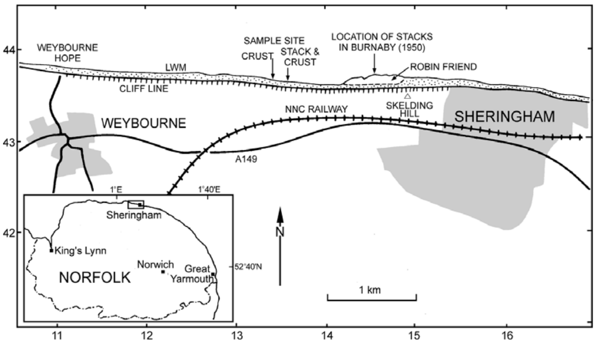


Figure 1. Sketch map showing location of the sample site and stacks described by Burnaby (1950). Numbered tick marks represent British national grid coordinates. 'Robin Friend' is an area of hard cemented chalk on the foreshore, almost certainly the base of former stacks.

occurred after deposition of the Wroxham Crag. The chalk here is also heavily brecciated, probably by periglacial (and possibly glacitectonic) processes, although individual flint bands can still be traced along strike (Pitchford, 1991).

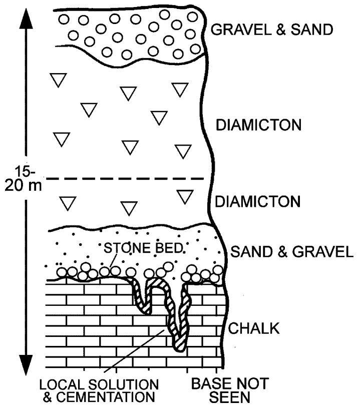
The Wroxham Crag Formation above the Chalk extends almost continuously along the section and comprises sands and gravels with inverse grading, and ripples with clay drapes and lenses, all features consistent with shallow marine deposition. The basal unit contains flint and some chalk cobbles and pebbles (the Stone Bed) and a marine bivalve and gastropod fauna. These sediments have been assigned to the Mundesley Member of the Wroxham Crag Formation (Rose, Moorlock & Hamblin, 2001; Pawley *et al.* 2004) of early Middle Pleistocene age. Apart from mollusc shells and local concentrations of chalk pebbles in the basal Stone Bed, the rest of the Wroxham Crag at Weybourne Hope is almost devoid of calcium carbonate material (Pawley *et al.* 2004).

Glacial sediments of the Sheringham Cliffs Formation and Briton's Lane Formation occur above the Wroxham Crag Formation. The Sheringham Cliffs Formation comprises contorted tills of the Runton Till and Weybourne Town Till members, which have calcium carbonate (mainly reworked chalk) contents ranging from about 10 to about 76 %, respectively (Lee *et al.* 2004; Pawley *et al.* 2004). The Briton's Lane Formation outwash sands and gravels are present as pockets of sediment at the cliff top near Weybourne Hope and capping Skelding Hill to the east of Sheringham (Lee *et al.* 2004).

2.a. The stacks and crust: field relations

The stacks exposed today are not *in situ*, the most recent having fallen over before the 1990s due to cliff retreat (Fig. 3a). The main stack studied was originally up to 4 m high and wide (Thurston & Whittlesea, 2002, fig. 1). Two vase-like structures, about 2 m wide and high, from the upper part of the stacks were found partially buried on the beach (Fig. 3b). On the inside surface of one wall of the 'vase', clear deposits of calcite flowstone (speleothem) were observed. A cemented crust of similar composition to the stacks is also found intermittently on parts of the upper surface of the Chalk underlying the basal bed of the overlying Wroxham Crag (Burnaby, 1950; Peake & Hancock, 1961, p. 315). The crust was observed *in situ* at two locations: one associated with the stacks, the other about 300 m to the west (Figs 1, 3c). The crust appears to be developed only where the overlying glacial tills contain large chalk rafts, and typically where these tills have 'down-cut' to within a few metres of the Chalk surface. The crust clearly contains inclusions of crag sediment, in places completely cementing flint pebbles; this shows (contrary to the view of Burnaby, 1950) that it formed after deposition of the crag. The crust originally passed laterally into the stacks (Burnaby, 1950), showing they were cemented at the same time. The upper surface of the crust shows crack-like brecciated structures in places (Fig. 3c), which Burnaby (1950) interpreted as sub-aerial desiccation cracks. While we agree that these cracks are shrinkage phenomena, we can see no evidence that they are sub-aerial features.

Although Burnaby (1950) describes reworked fragments of angular cemented chalk within the crag deposits at West Runton, we think he was mistaken. We have observed what appear to be crust fragments within the Stone Bed at Weybourne, but these can be traced laterally into the crust and are actually crust-like



BRITON'S LANE SAND AND GRAVEL MEMBER	BRITON'S LANE FORMATION	LATE PLEISTOCENE
WEYBOURNE TOWN TILL MEMBER	SHERINGHAM CLIFFS FORMATION	MIDDLE PLEISTOCENE
RUNTON TILL MEMBER		
MUNDESLEY MEMBER	WROXHAM CRAG FORMATION	EARLY MIDDLE PLEISTOCENE
WEYBOURNE CHALK MEMBER	NORWICH CHALK	UPPER CRETACEOUS (CAMPANIAN)

Figure 2. Summary of lithostratigraphy and schematic log of sediments in the Sheringham-Weybourne cliffs.

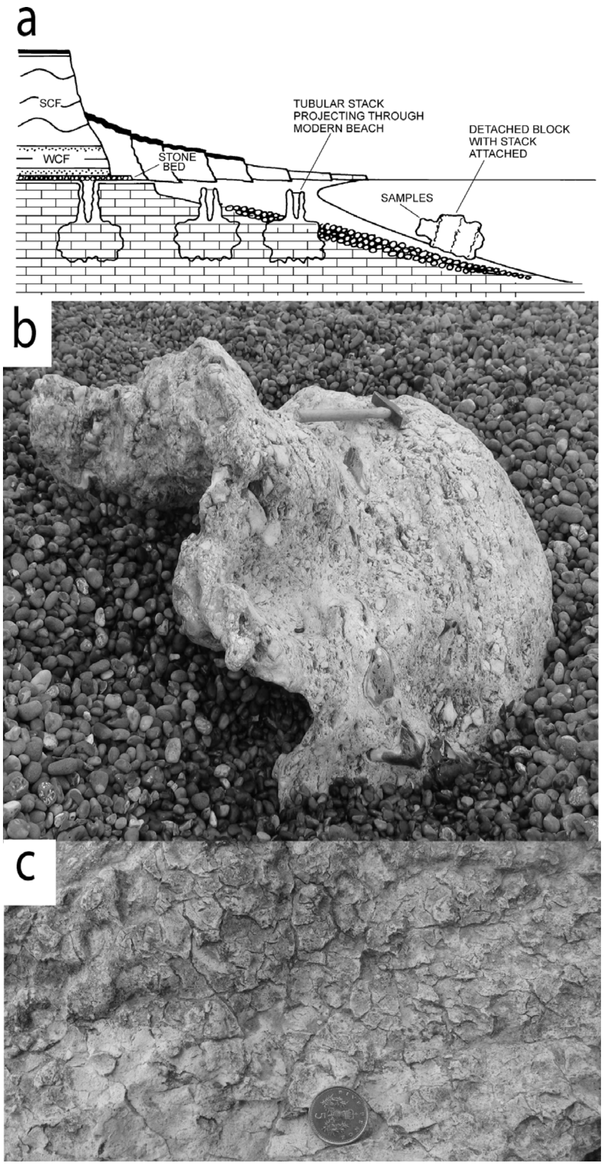


Figure 3. (a) Schematic diagram (after Burnaby, 1950) to show original attitude of the stacks and their erosion during cliff retreat. The bases of the cemented blocks at the base of the stacks probably coincided with the groundwater table at the time of stack formation. Samples for this study came from the upper parts of detached stacks as indicated. WCF – Wroxham Crag Formation; SCF – Sheringham Cliffs Formation. Field photographs show (b) upper part of cemented vase-like stack structure, partially buried in modern beach sediment, August 2005 (hammer handle 0.35 m long) and (c) the cemented crust on the chalk surface with cracked and brecciated areas, January 2008; coin diameter is 17 mm.

coatings on chalk pebbles; we are confident these formed within the crag sediment nucleating on chalk substrates.

All of the field evidence discussed above shows that both karstification and cementation occurred after deposition of the Wroxham Crag.

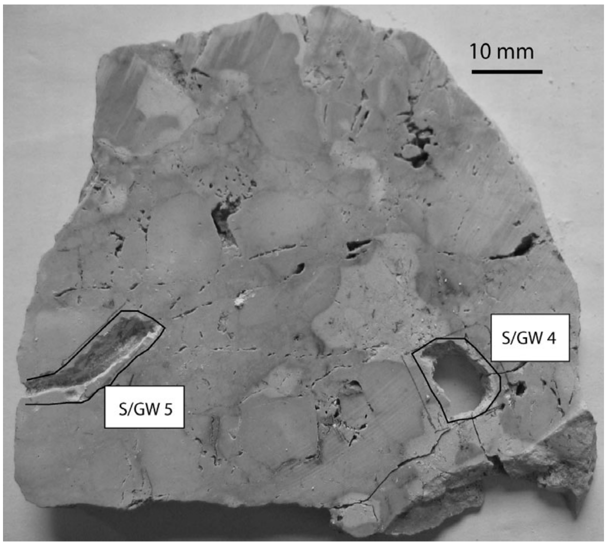


Figure 4. Slabbed hand specimen from stack wall showing brecciated fabric with well-cemented (darker grey areas) and uncemented (lighter) areas. Black lines mark isotope sample areas (S/GW 4 bottom right, uncemented; δ^{18}O −2.6 ‰, δ^{13}C −0.7 ‰ and S/GW 5 bottom left, cemented; δ^{18}O −3.4 ‰, δ^{13}C −3.3 ‰) illustrating the scale of isotopic variability within a hand specimen.

3. Methods

Hand specimens were collected from representative material of: (1) cemented stack walls and crusts (hereafter cemented chalks, Fig. 4); (2) apparently uncemented chalks typically included within the cemented areas (hereafter uncemented chalks, Fig. 4); and (3) chalks some metres from the stacks (hereafter unaltered chalks). These were then sub-sampled for thin-sections, scanning electron microscopy (SEM), density measurements and geochemistry. SEM samples were cut from hand specimens, then crushed in a rock splitter to expose fracture surfaces. Carbon coating was used for EDS elemental analysis, then samples were re-coated in gold for high-resolution morphology study.

Geochemical samples were taken with a dental drill from a range of cemented and uncemented areas. Partially cemented areas were avoided as their degree of cementation was uncertain. For trace elements, about 500 mg of dried homogenized sample were dissolved in 20 ml of 10 % acetic acid, as trials showed that dilute acetic acid caused minimal leaching of elements from acid insoluble residues (IR). Solutions were then filtered with an in-line syringe GFC filter and made up to 100 ml. Trace elements were determined using a Varian Vista pro CCD simultaneous ICP-AES. The ICP data were drift and blank corrected; mean 1σ standard deviations of 12.3 ppm (Mg), 3.3 ppm (Sr), 4.5 ppm (Mn) and 9.7 ppm (Fe) were propagated from weighing errors and errors associated with the ICP concentration-intensity regression. Insoluble residue (wt % IR) was calculated from the dried mass on the filter.

For stable isotope analysis, volatile organic matter was removed from calcites by low-temperature ($< 80\,^{\circ}$C) oxygen plasma ashing for three hours at 300 W forward power in a Bio-Rad PT 7300 plasma barrel etcher. A 150 μg sub-sample was then reacted with anhydrous H_3PO_4 at 90 °C in an automated ‘common acid bath’ preparation system, and isotope ratios were measured on a Europa SIRA Hybrid mass spectrometer. Repeated analyses of the laboratory standard ($n = 14$) gave a 2σ precision of ± 0.09 ‰ for carbon and ± 0.08 ‰ for oxygen.

For ten samples, intact dry density (hereafter density) and stable isotopes were measured on the same block.

Density was measured on 1 cm^3 (edges measured with callipers) blocks cut from hand specimens. Block volume was calculated by multiplying the average x, y and z lengths for the block. Isotope samples were taken from the centre of block faces.

4. Results

The very fine-grained chalk matrix and microsparry cement crystals meant that thin-sections were of limited value for discerning differences in texture between cemented and uncemented chalk (a problem also noted by Burnaby, 1950). SEM study allowed better resolution. Cemented chalks from the stacks and crusts have low porosity and sharp blocky textures due to the interlocking of subhedral calcite overgrowths. Uncemented and unaltered chalks have a more granular structure with occasional coccoliths. The boundary between cemented/uncemented chalk in the stack samples, although apparently sharp in hand specimen (Fig. 4), is gradational under the SEM. Coccoliths in the cemented chalk are well preserved, although they may be partly overgrown by neomorphic calcites. Fractures in the cemented chalk are typically lined with euhedral calcite microspar crystals exhibiting rhombohedral and scalenohedral habits. The cemented chalks do not show any petrographic or SEM fabrics (e.g. spar coronas, needle-fibre calcites) indicative of a pedogenic or rhizogenic origin (cf. Strong, Giles & Wright, 1992; Candy, 2002; Candy, Rose & Lee, 2006). Chalk density increases dramatically (Fig. 5) from unaltered chalks (~ 1.7 mg m^{-3}) to cemented chalks (~ 2.6 mg m^{-3}).

The geochemical data is summarized in Table 1. Stable isotope values ($\delta^{13}C \sim +2$ and $\delta^{18}O \sim -2$ ‰ respectively) for unaltered chalk and belemnites are similar to those from Campanian Chalks in the nearby Trunch borehole core (Jenkyns, Gale & Corfield, 1994; McArthur, 1995). However, both $\delta^{13}C$ and $\delta^{18}O$ decrease (to values around −4 and −3.7 ‰, respectively) with increasing cementation (Figs 4, 6) and density (Fig. 5). The most negative isotope values

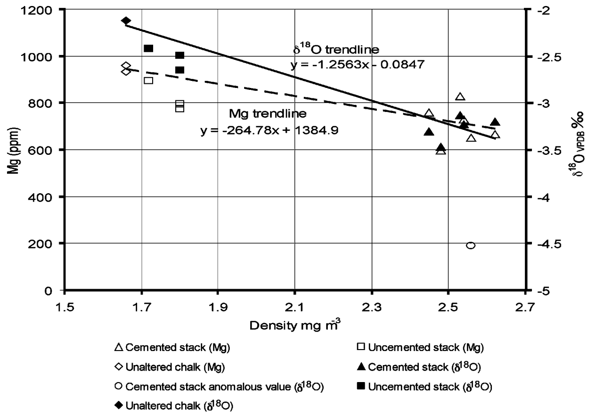


Figure 5. Sample density plotted against $\delta^{18}O$ values and Mg concentration. The anomalously low $\delta^{18}O$ value is probably due to a higher proportion of fracture-filling cement in the sample. The $\delta^{13}C$ data show a similar relationship with density (see also Fig. 6) but are omitted from the plot for clarity.

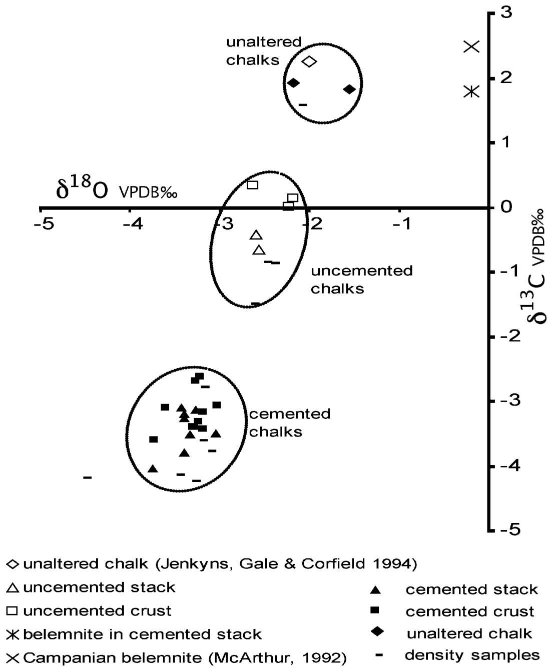


Figure 6. Stable isotope data from this study plotted with relevant comparative data. The data fall into three main groups, unaltered chalks and fossils having the highest values and cemented chalks from the stacks and crusts having the lowest values. Uncemented chalks from the stacks and crusts have values intermediate between the other two groups.

Table 1. Summary of geochemical data

Lithology	$\delta^{18}O$ ‰$_{VPDB}$	$\delta^{13}C$ ‰$_{VPDB}$	Mg (ppm)	Sr (ppm)	Mn (ppm)	Fe (ppm)	Wt % IR
Cemented stack	−3.42 ± 0.37	−3.59 ± 0.46	692 ± 86	500 ± 70	112 ± 28	688 ± 326	1.4 ± 0.47
Uncemented stack	−2.55 ± 0.09	−0.86 ± 0.40	803 ± 49	549 ± 91	128 ± 12	861 ± 171	2.0 ± 0.78
Cemented crust	−3.31 ± 0.21	−3.18 ± 0.32	575 ± 135	447 ± 105	109 ± 34	1401 ± 1878	11.0 ± 14.7
Uncemented crust	−2.34 ± 0.24	+0.17 ± 0.17	764 ± 208	565 ± 87	149 ± 35	2204 ± 1430	11.0 ± 13.8
Unaltered chalk	−1.95 ± 0.35	+1.77 ± 0.17	973 ± 47	629 ± 28	193 ± 18	514 ± 50	< 2.0
Belemnite in cemented stack	−0.19	+1.8	904	1009	37	154	–

Sample sizes vary from a minimum of 3 (unaltered chalk) to maximum of 13 (cemented stack), except the belemnite data which is from a single sample. The high insoluble residue (wt % IR) and Fe data in the crust samples are due to incorporation of crag sediment in the crusts.

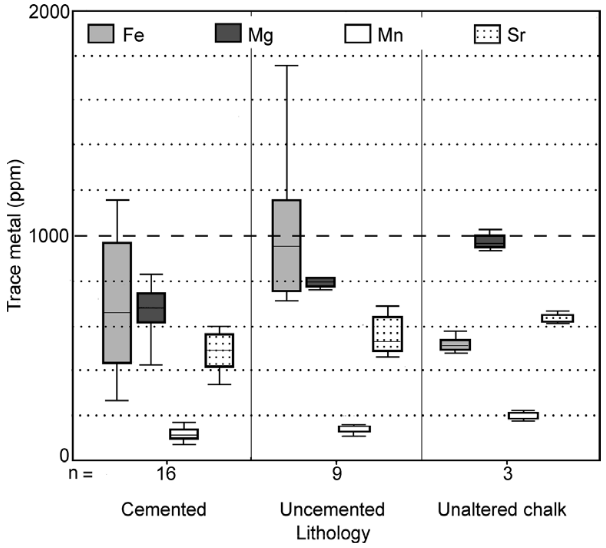


Figure 7. Trace element data box and whisker plot. For each parameter the bar in the central shaded box represents the mean, the ends of the shaded boxes represent the 25th and 75th percentiles and the bars at the ends of the thin lines represent the 10th and 90th percentiles.

come from samples with microspar-cemented fracture porosity.

Means of the trace element concentrations (Sr, Mg, Fe, Mn) from sub-samples of unaltered, cemented and uncemented chalks are shown in Figure 7. Sr concentrations in the unaltered samples (629 ± 28 ppm) are similar to other Norfolk Chalk data (690 ± 130 ppm: Scholle, 1977; 590 ppm: McArthur, 1995). Mg values for unaltered chalks in this study (973 ± 47 ppm) are, however, lower than equivalent data in Norfolk (1800 ± 320 ppm: Scholle, 1977) and North Sea (1960 ± 530 ppm: Scholle, Albrechtson & Tirsgaard, 1998) chalks.

Mean Mg and Mn concentrations were significantly lower (t-test at the 0.05 confidence level) in cemented versus uncemented chalks, whereas Sr and Fe were not significantly different. In the cemented chalks, Sr and Mg are the most strongly statistically correlated trace elements (Fig. 8), while Mn is correlated with Sr and Mg to a lesser extent. Mg concentration also clearly decreases with sample density (Fig. 5).

Cemented and uncemented chalks from the stacks typically contained between 1 and 3 wt % insoluble residues (IR) and were not statistically different from one another. Some of the cemented crusts, however, had included between 5 and 40 % Wroxham Crag material (Table 1).

5. Geochemistry and density data interpretation

Overall, the Chalk geochemical data show more negative stable isotope values and lower Mg and Sr values as the samples become more cemented. These trends, combined with the field evidence for chalk cementation being related to solution phenomena, are broadly consistent with dissolution and cementation being driven by meteoric groundwater, sourced from above. There is no petrological evidence that the cementation is related to either pedogenic or rhizogenic processes. The more negative $\delta^{18}O$ values in the cemented chalks are consistent with meteoric water involvement and the more negative $\delta^{13}C$ values sourced from soil-CO_2 (see Discussion below). Lower Mg concentrations in the chalks generally may be indicative of Mg leaching due to the proximity of an exposure surface (the regional Chalk–Wroxham Crag unconformity), while the lower Mg and Sr values in the cemented chalks suggest either neomorphism and leaching of the chalk matrix, or precipitation of cements with lower Mg and Sr concentrations than the chalks. The Fe and Mn data are mainly related to the presence of iron-manganese oxides on micro-crack surfaces (confirmed by SEM-EDS analysis) and are not considered further here.

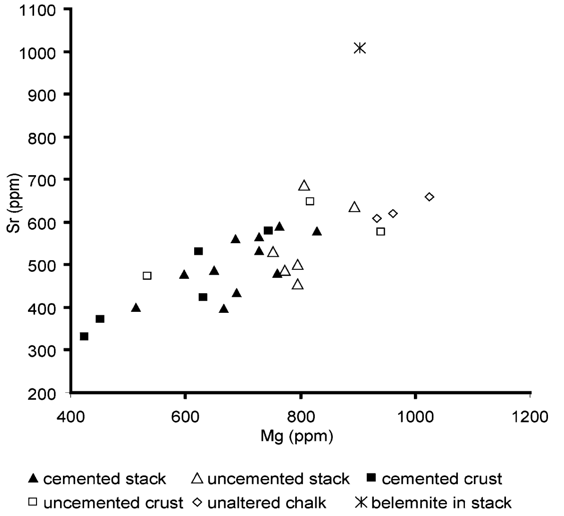


Figure 8. Cross-plot of Mg and Sr data showing strong linear covariance in the chalk data.

The increase in density from unaltered chalk (~ 1.6 mg m^{-3}) to cemented chalk (~ 2.65 mg m^{-3}) resulted from either the infilling of porosity by cement, or compaction. As neither we nor Burnaby (1950) saw any physical evidence for differential compaction of the cemented chalks, we conclude that the density increase is largely due to cementation of pore space by calcite cements leaving a residual 0–3 % porosity (see also Burnaby, 1950). The decrease in $\delta^{18}O$ with increasing density is wholly consistent with the presence of a meteoric cement filling pore spaces, and by comparing the density of cemented and unaltered chalk, the proportion of this cement can be estimated, which in turn allows calculation of the cement geochemical parameters.

5.a. Calculating $\delta^{18}O$ of the cement

To calculate $\delta^{18}O$ of the cement, we used slightly different scenarios as a sensitivity test. Scenarios 1 and 2 (Table 2) both assume the infilling of unaltered chalk porosity by cement; however, in scenario 1 the mean isotopic data for more weathered chalk was

Table 2. Scenarios for cementation and resulting cement stable isotope compositions based on means of measured density and isotopic data

Scenario	Description	Uncemented chalk density (mg m^{-3})	Cemented chalk max. density (mg m^{-3})	δx ‰ $_{\text{VPDB}}$ cemented chalk**	δx ‰ $_{\text{VPDB}}$ uncemented chalk	δx ‰ $_{\text{VPDB}}$ cement
1	Cementation of unaltered weathered chalk	1.66*	2.62	δ^{18}O −3.26 δ^{13}C − 3.79	δ^{18}O −1.55 δ^{13}C +1.92	δ^{18}O − 6.23 δ^{13}C − 13.67
2	Cementation of unaltered fresh chalk	1.66*	2.62	δ^{18}O − 3.26 δ^{13}C − 3.79	δ^{18}O − 2.12 δ^{13}C +1.58	δ^{18}O − 5.24 δ^{13}C − 13.08
3	Cementation of uncemented stack/crust	1.77	2.62	δ^{18}O − 3.26 δ^{13}C − 3.79	δ^{18}O − 2.52 δ^{13}C − 1.08	δ^{18}O − 4.82 δ^{13}C − 9.49

*unaltered chalk; **δ^{18}O values are mean of density samples excluding one anomalous value.

used, whereas in 2 the isotope data for fresher chalk was used. In scenario 3 (Table 2), we assume the chalk to be cemented has already been partially altered by limited dissolution/re-precipitation reactions (that is, the 'uncemented' stack material described above). These data were then put into a mixing equation of the following type:

$$\delta^{18}\mathrm{O}_{\text{cement}} = \delta^{18}\mathrm{O}_{\text{uncemented chalk}} + \left[\frac{\left(\delta^{18}\mathrm{O}_{\text{cemented chalk}} - \delta^{18}\mathrm{O}_{\text{uncemented chalk}}\right)}{\left(1 - \left(\frac{\text{density}_{\text{uncemented chalk}}}{\text{density}_{\text{cemented chalk}}}\right)\right)} \right]$$

Table 2 shows the values used in the equation and the calculated $\delta^{18}\mathrm{O}_{\text{cement}}$ ($\delta^{13}\mathrm{C}_{\text{cement}}$ was calculated using the same equation and assumptions). The unaltered chalk density equates to a porosity of 37 %, comparable to a published value of 40 % for Norfolk Chalk (Scholle, 1977). The maximum cemented chalk density (2.62 mg m^{-3}) agrees with data in Burnaby (1950) and represents cemented chalk with the lowest fracture porosity. The mean $\delta^{18}\mathrm{O}_{\text{cemented chalk}}$ of −3.3 ‰ (1σ 0.13 ‰) from the density samples excludes an anomalously low value (Fig. 5) The mean $\delta^{13}\mathrm{C}_{\text{cemented chalk}}$ from the density samples was −3.8 ‰ (1σ 0.13 ‰).

The results in Table 2 suggest that the cements have a δ^{18}O between −4.8 to −6.2 ‰ and a δ^{13}C between −9.5 and −13.6 ‰, depending on scenario. Scenario 3 is probably the most realistic geologically and results in the heavier isotopic compositions (δ^{18}O −4.8 ‰; δ^{13}C −9.5 ‰). A δ^{18}O of −4.8 to −6.2 ‰ for the cement is broadly consistent with calcite precipitation from meteoric water under present-day climatic conditions, the mean for δ^{18}O for British calcitic tufa deposits from groundwater-fed streams being −5.8 ‰ (Andrews, Riding & Dennis, 1993). Middle Pleistocene East Anglian pedogenic calcretes, interpreted to have formed under warmer, seasonally dry climates, have δ^{18}O between −3.6 and −4.9 ‰ (Candy, Rose & Lee, 2006), the more negative values probably being least evaporated. Groundwater calcretes (Fig. 9) seen on the upper surfaces of the Wroxham Crag at nearby West Runton have a δ^{18}O of −5.1 ‰. The negative δ^{18}O values cannot be generated by the 'organic dissolution of chalk' mechanism proposed by Burnaby (1950), as this requires carbonate sourced from dissolution of the chalk itself, which cannot generate δ^{18}O values much below −2 ‰.

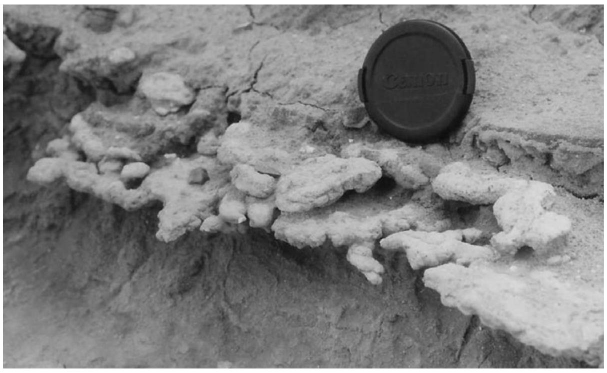


Figure 9. Platy-nodular groundwater calcrete forming at the junction of the Wroxham Crag Formation and Sheringham Cliffs Formation sediments. Lens cap 50 mm diameter for scale. W side of slipway, Woman Hythe, West Runton.

The very low δ^{13}C values for the cements are consistent with calcite precipitated from groundwaters with dissolved carbon sourced from biological respiration of C3 organic matter and open system dissolution of calcium carbonate. Modern Norfolk glacial till groundwater has dissolved inorganic carbon (DIC) δ^{13}C values around −21.3 ‰ (Feast *et al.* 1997), which at modern groundwater temperatures, and known empirical fractionation effects between DIC and $CaCO_3$ (e.g. Emrich, Ehhalt & Vogel, 1970), could precipitate calcite with values as negative as −11 ‰. The most negative δ^{13}C for modern British calcitic tufa deposits from groundwater-fed streams is −11.9 ‰ (Andrews, Riding & Dennis, 1993), and values below this (e.g. −13 ‰ in Dever *et al.* 1983) are rare in nature. Overall this suggests that the −9.5 ‰ estimate for the cements described here (Table 2) is likely to be the more realistic. The open system conditions implied by these negative δ^{13}C cement values suggest that carbonate dissolution and respiration of organic matter occurred in unconfined hydrogeological conditions, almost certainly in the soil and siliciclastic glacial deposits that overlie the chalk and crag deposits. Groundwater calcretes (Fig. 9) observed on the upper surfaces of the Wroxham Crag at nearby West Runton formed by exactly these processes and have a δ^{13}C of −8.7 ‰, close to the predicted cement value

Table 3. Calculated temperatures and minimum groundwater $\delta^{18}O$ compositions

$\delta^{18}O$ ‰$_{VSMOW}$ water (assumed)	$\delta^{18}O$ ‰$_{VPDB}$ cement (calculated)	T (°C)
−7.0 (mean modern Norfolk groundwater)	−6.2 (Scenario 1, Table 2) −4.8 (Scenario 3, Table 2)	12.3 6.7
−9.5 (mean end-Pleistocene Norfolk groundwater)	−6.2 (Scenario 1, Table 2) −4.8 (Scenario 3, Table 2)	2.7 −2.1
−10.3*	−6.2 (Scenario 1, Table 2)	0
−8.9**	−4.8 (Scenario 3, Table 2)	0

Calculations based on scenarios 1 and 3 (Table 2) and using the Hays & Grossman (1991) palaeotemperature equation. $\delta^{18}O$ values for modern Norfolk and end-Pleistocene (pre-Holocene recharge) groundwaters from Hiscock *et al.* (1996) and Darling (2004). Water $\delta^{18}O$ values marked * and ** represent minimum values from scenario 1 and 3 cement compositions before freezing temperatures are calculated.

of −9.5 ‰. Other British Middle–Late Pleistocene pedogenic calcretes have similar $\delta^{13}C$ values, in the range −8.5 to −11.0 ‰ (Strong, Giles & Wright, 1992; Candy, Rose & Lee, 2006). As these relatively negative compositions implicate biological respiration in the soil, they show that cementation occurred under active soil-forming, not glacial or permafrost, conditions (cf. Dever *et al.* 1983; Lacelle, 2007).

5.b. Settings limits on palaeotemperature and groundwater isotopic compositions

The $\delta^{18}O$ of calcite precipitated from a solution is a function of both the temperature at which the calcite precipitated and the $\delta^{18}O$ of the solution. If the calcite precipitates in isotopic equilibrium with the solution, then a predictable relationship exists between temperature, $\delta^{18}O_{calcite}$ and $\delta^{18}O_{solution}$. For meteoric cements the Hays & Grossman (1991) equation is the most appropriate:

$$T = 15.7 - 4.36(\delta c - \delta w) + 0.12(\delta c - \delta w)^2$$

where T = temperature of calcite precipitation (°C), $\delta_c = \delta^{18}O_{calcite}$‰ VPDB and $\delta_w = \delta^{18}O_{water}$‰ VSMOW. As we have calculated δ_c values, an estimation of δ_w allows a temperature estimate to be made. Groundwater $\delta^{18}O$ is determined largely by the $\delta^{18}O$ of meteoric water, and modern north Norfolk Chalk groundwaters have a $\delta^{18}O$ composition close to −7 ‰ VSMOW (Hiscock *et al.* 1996). Freshwaters that entered the Chalk during brief interstadial periods of the Devensian glaciation have been identified, trapped beneath glacial deposits in interfluve areas of the aquifer, and have $\delta^{18}O$ compositions down to −8.2 ‰ VSMOW (Hiscock *et al.* 1996; Feast *et al.* 1997). These palaeowaters, however, may not represent last glacial recharge compositions, having been modified by diffusion and downward infiltration of modern meteoric waters, and mixing with deeper saline water. Other estimates of late Pleistocene, before Holocene recharge, compositions of UK groundwaters suggest a $\delta^{18}O \sim -9.5$ ‰ VSMOW (Darling, Edmunds & Smedley, 1997; Darling, 2004). On this basis, calcite precipitation temperatures (Table 3) can be constrained to no warmer than 12 °C (temperatures similar to modern mean Norfolk groundwater temperatures; e.g. see Hiscock, 1991), although possibly colder. The $\delta^{18}O_{water}$ cannot have been less than about −9 to −10 ‰ (depending on scenario), as the resulting temperatures (Table 3) are below freezing point. This latter estimate almost certainly excludes input of much isotopically depleted water from melting glaciers, which were certainly present in the study area at times during the Pleistocene.

It is interesting to note that while significantly isotopically depleted glacial meltwaters must have been common during large periods of the Devensian glaciation, there is no published evidence of recharge from such waters in British aquifers or in palaeowater archives such as speleothems. Unpublished work on a British speleothem by T. C. Atkinson and P. J. Rowe (pers. comm. 2008) suggests that full glacial British precipitation could have been depleted by as much as 15 ‰ in ^2H with respect to modern waters. This is consistent with a $\delta^{18}O$ composition of approximately −9.5 ‰$_{VSMOW}$ for end-Pleistocene groundwater (Atkinson, 2004; Darling, 2004).

6. Discussion and conclusion

The geochemical data presented here preclude a marine origin for chalk cementation, and show conclusively that the driver was meteoric-sourced groundwater, supersaturated with calcium carbonate and derived from biologically active soils. As a source of dissolved calcium carbonate to groundwater is required, it is most likely that reworked chalk in the overlying glacial tills of the Sheringham Cliffs Formation was the dominant source: the observed relationship between presence of crust and overlying chalk-rich tills supports this interpretation. As these tills were probably deposited during MIS 12 (Pawley *et al.* 2008), the cementation is unlikely to be older than *c.* 480 ka (much younger than the timing proposed by Burnaby, 1950). This is strongly supported by the nearby presence of groundwater calcretes at the contact between the Sheringham Cliffs Formation tills and the Wroxham Crag (Fig. 9). These calcretes can only have formed from calcium carbonate dissolved from the overlying tills. Secondly, in places, the lower and basal beds of the Wroxham Crag between Weybourne and West Runton contain mollusc shells, which, although altered (typically chalkified) to some degree, are quite well preserved and retain original aragonite mineralogy (verified by X-ray diffraction). These aragonite shells have survived post-crag dissolution in places, mainly because they have been protected from groundwater dissolution by clay beds and laminae, but perhaps also because groundwater infiltrating the sands and gravels was in places already supersaturated with calcium carbonate to the point of aragonite insolubility. It seems likely that local calcium carbonate supersaturation of groundwater was driven by the local presence of chalk rafts in the overlying glacial tills.

The negative carbon isotope compositions are indicative of biologically active soils, and this precludes glacial or permafrost conditions. On this basis we infer that cementation occurred under warm climatic conditions, probably during an interglacial, although the $\delta^{18}O_{calcite}$ values imply conditions no warmer than the present day.

We conclude that the intermittent occurrence of stacks along-section is related to the locus of solution features which strongly influenced local hydrogeological flow paths. The solution features clearly post-date deposition of the Wroxham Crag, and it is quite likely they were caused by routing of sub-glacial water, or glacial melt-water. Although the study site is close to the Devensian ice margin, there is no proof positive that solution was a Devensian event. Indeed the nearby glacial outwash deposits of the Briton's Lane Sand and Gravel Member appear to be of MIS 12 age (Pawley *et al.* 2008), so solution could have been related to these outwash events. We can be more certain, due to the isotopic constraints, that cementation was not related to glacial melt-water or subglacial waters. Cementation was localized in areas of low topography on the chalk surface (pre-existing solution features), was related to remobilization of calcium carbonate from the overlying glacial tills and occurred at a time when soils were biologically active, suggesting an interglacial after MIS 12; it is not possible to be more specific regarding the timing of cementation.

In a wider context this study shows the value of detailed investigation into the geochemistry of near-surface cements as palaeohydrological/climatic indicators. It is likely that other solution-related cementation in both Chalk (e.g. calcrete-cemented solution pipes in the Sussex Chalk: Mortimore, 1997, pp. 61–2) and non-Chalk settings will prove equally interesting.

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