Environments of the climatic optimum of MIS 11 in Britain: evidence from the tufa sequence at Hitchin, southeast England

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ABSTRACT: Marine Oxygen Isotope Stage 11 (MIS 11, Hoxnian Interglacial) is an important interval for understanding both climate change in an interglacial partially analogous to the Holocene and the response of geomorphic processes, biotic systems, and hominin populations to these changes. In Britain, many sites correlated to MIS 11 have not been studied since the mid-20th century and require reinvestigation, including the Hitchin tufa sequence, where a rich, non-marine molluscan assemblage was originally recovered. Re-excavation of the Hitchin tufa sequence for this study was focussed on combined sedimentological, micromorphological, and geochemical analyses of the deposits. These indicate that tufa formation occurred within a perched springline system under temperate climatic conditions. Shifts between paludal to fluvial tufa facies within this system occur concomitantly with changes in carbonate geochemistry, representing increased humidity caused by a change in rainfall amount or seasonality. This research enables a correlation of the sequence to the climatic optimum of MIS 11c, the main warm phase of MIS 11, and permits further insights into temperature and hydrological changes in this interval by generating the first geochemical records of hydroclimatic evolution during the MIS 11 thermal maximum in Britain.

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KEYWORDS: Hoxnian Interglacial; Middle Pleistocene; MIS 11; stable isotopes; tufa; trace elements

Introduction

Given the importance of Marine Oxygen Isotope Stage (MIS) 11 (ca. 425–360 ka) for our understanding of interglacial climate complexity (EPICA, 2004; Jouzel et al., 2007; Stein et al., 2009; Tzedakis et al., 2009; de Beaulieu et al., 2001; Koutsodendris et al., 2012 Candy et al., 2014; Tye et al., 2016), the palaeogeographic evolution of northwest Europe (Gibbard, 1995; Meijer and Preece, 1995; Gupta, 2007; White et al., 2013; Gibbard and Cohen, 2015), and the Middle Pleistocene archaeological record (Wymer, 1988; Bridgland 1994; White and Schreve, 2000; Ashton et al., 2006; White et al., 2019), detailed studies of continental records of this interglacial are crucial for understanding environmental change. Britain preserves numerous terrestrial sequences that have been correlated with MIS 11 on the basis of lithostratigraphic (Bowen et al., 1986; Bridgland, 1994, 2000), biostratigraphic (Keen, 2001; Schreve, 2001a) and geochronological techniques (Rowe et al., 1999; Preece et al., 2007; Perelman et al., 2011, 2013). These sequences have revolutionised our understanding of how climatic variability is recorded in the terrestrial record and its impact on geomorphic systems, biota and hominin populations. Climatic reconstructions from British MIS 11 sequences have relied principally on pollen analysis and biologically derived temperature estimates (Candy et al., 2010; Coope, 2010). However, many of these sequences are also rich in biogenic and abiogenic carbonates, where geochemical techniques can be applied to yield further climatic information.

Tufa deposits are accumulations of carbonate precipitated at ambient water temperature in riverine and lake shoreline settings (Pedley, 1990; Viles, 2004; Pentecost, 2005; Capezzuoli et al., 2014). Although often fragmented, the calcareous nature of these sequences makes them highly suitable archives of stable isotope and trace element information. They also readily preserve molluscan and vertebrate remains, from which both climatic and ecological changes can be inferred (see Dabkowski, 2014 and references therein). In continental Europe, the utility of these deposits for reconstructing terrestrial climate change during MIS 11 has been demonstrated by several detailed studies (Rousseau et al., 1992; Kahlke, 2002; Limondin-Lozouet and Antoine, 2006; Dabkowski et al., 2012); however, in Britain, only one such sequence of this age, Beeches Pit at West Stow, Suffolk, has been extensively studied (Preece et al., 1991, 2006, 2007). The only other tufa sequence in Britain that has been correlated with MIS 11 is preserved near Hitchin, Hertfordshire. The Hitchin sequence, first described by Kerney (1959), is best known for its rich molluscan assemblages and a small assemblage of vertebrate remains, but despite its potential to elucidate environmental changes during MIS 11, little further work has been undertaken since the 1950s. Consequently, new sections were exposed in 2013 with the aim of furthering our understanding of the mode and environmental context of tufa formation at Hitchin.

This paper describes the results from this re-excavation, focusing specifically on combined sedimentological, micromorphological, and geochemical (δ18O, δ13C and trace element (Ca, Mg, Sr) analyses. We first discuss the results of sedimentology and micromorphology, producing a model of tufa formation at the Hitchin locale, before going on to discuss the geochemical data, which can be interpreted in terms of prevailing temperatures and rainfall at the time of tufa.
form. These data provide evidence for hydroclimatic and landscape change during the climatic optimum of MIS 11c in Britain which is then placed in the wider context of environmental changes in Britain and northwest Europe.

Background and study area

Stratigraphy of MIS 11 deposits in Britain and northwest Europe

The Hitchin tufa sequence is one of a corpus of sites in Britain that has been attributed to the Hoxnian Interglacial (West, 1956; Turner, 1970; Coxon, 1985; Bridgland, 1994; Schreve et al., 2001a, 2001b; Ashton et al., 2005; Preece et al., 2006, 2007; Coope and Kenward, 2007; Ashton et al., 2008). Through a combination of biostratigraphic, geochronological and lithostratigraphic techniques, this temperate episode has been correlated with MIS 11; more specifically the main temperate phase of the interglacial, MIS 11c (for a detailed review, see Candy et al., 2014 and references therein). The Hoxnian Interglacial is sub-divided into four substages, HoI–HoIV, on the basis of pollen biostratigraphy (Turner, 1970; Coxon, 1985; Ashton et al., 2008). Hollla–b, the late temperate zone, is suggested to correlate to the climatic optimum of MIS 11c based on alignment of the Hoxnian pollen stratigraphy to sea-surface temperature records (Candy et al., 2014). This alignment is supported by palaeoecological and geochemical evidence from several sequences spanning Hollla–b in Britain (Tye et al., 2016; Bridgland et al., 1999; Ashton et al., 2008) which indicate relatively warmer temperatures during HoII in comparison with Holll and HoVI.

Of particular relevance to this study is the occurrence of the age-diagnostic mollusc group, the ‘Lyrodiscus assemblage’ in Hoxnian Interglacial deposits. The group represents a distinctive suite of taxa representing forest environments (Rousseau et al., 1992; Antoine and Limondin-Lozouet, 2004; Limondin-Lozouet and Antoine, 2006; Limondin-Lozouet et al., 2006, 2020; Clquiet et al., 2009), and includes species representing warmer and more humid conditions than the present day (Rousseau, 2003; Preece et al., 2007). The Lyrodiscus assemblage has been identified in a series of independently dated MIS 11 tufa deposits including Beeches Pit in Britain (Fig. 1; Preece et al., 2007) and Saint Pierre-lès-Elbeuf (Clquiet et al., 2009; Voinchet et al., 2015), Vernon (Lécolle et al., 1990; Rousseau et al., 1992) and La Celle (Limondin-Lozouet et al., 2006; Dabkowski et al., 2012, Voinchet et al., 2015) in France. Combined malacological and isotopic records from the La Celle tufa sequence indicate that the emergence and persistence of the Lyrodiscus assemblage corresponds to isotopic evidence representing higher temperatures during MIS 11c (Dabkowski et al., 2012). Through means of mollusc biostratigraphy (see Preece et al., 2007 and White et al., 2013 for detailed reviews), the occurrence of the Lyrodiscus assemblage at Beeches Pit has been correlated to Hollla–b. Together, the evidence from La Celle and Beeches Pit indicates that the occurrence and persistence of the Lyrodiscus assemblage may therefore act as a stratigraphic marker for the climatic optimum of MIS 11c in western Europe.

Hitchin tufa site context

The tufa sequence at Hitchin (51°57′17.60″N, 000°17′43.04″W, 70 m OD) is located c. 1 km northwest of Hitchin, Hertfordshire (Fig. 1). It forms part of the Oughtonhead Lane Site of Special Scientific Interest (SSSI) on the southern flank of a small valley at the head of the River Oughton. The active spring (Oughton Head) that supplies the River Oughton lies c. 1 km west of the tufa sequence at an elevation of 63 m OD. The tufa sequence itself lies near the contact between the Cretaceous chalk bedrock that forms the Oughton Valley and Quaternary glaciofluvial deposits associated with the western margin of the Hitchin Channel, formed during the Anglian glaciation (Hopson et al., 1996, Fig. 1). It is important to note that the Hitchin tufa sequence is distinct from the series of lacustrine sequences in the Hitchin area which collectively form the Hitchin ‘lake beds’ including the sequences found at Maydencroft Manor, Jeeve’s Pit and Fisher’s Green (Gibbard, 1977; Boreham and Gibbard, 1995). These sequences have also been correlated with the Hoxnian Interglacial on the basis of lithostratigraphy and pollen biostratigraphy, with layers of decalcified lacustrine sediments that are present in the sequences suggested to represent a

Figure 1. Location maps of the study area. (A) Regional maps showing key MIS 11 sites discussed in the text. (B) Location of the Hitchin tufa excavated as part of this study (H13-TP2) in relation to previously described section by Kerney (1959). Quaternary geology, and the approximate position of the Hitchin Channel (based on BGS 50k superficial geology). [Color figure can be viewed at wileyonlinelibrary.com].
former ‘Hoxnian land surface’ extending southwards along the Hitchin Gap (Hopson et al., 1996). Based on our current stratigraphic understanding, it is unclear how these ‘lakebed’ deposits correlate with the Hitchin tufa sequence.

**Previous excavations at Hitchin**

The Hitchin tufa sequence was first identified by Wiggs (1943, 1944, 1945), who described a sequence (from the base upwards) of light brown glacial clay, tufa, peat and glacial clay with sands and stones. These early investigations of the tufaceous deposits yielded 11 species of terrestrial mollusc that Wiggs correlated with the High Terrace deposits of the Thames (the Boyll Hill/Orsett Heath Terraces as described by Bridgland, 1994). The sequence was re-excavated by Kerney (1959) who described a comparable sediment sequence, forming (from the base upwards) glacial outwash, carbonate-rich colluvium, tufa, and glacial meltwater gravel. Together, the tufa (Unit C) and underlying colluvial deposit (Unit B) excavated by Kerney, represented a thickness of approximately 0.5 m.

A single bulk sample from each of these units was analysed for molluscan remains. Unit B comprised a less diverse fauna than Unit C, represented principally by the terrestrial taxa with a small freshwater component (Table 1). Unit C comprised high abundances of a range of terrestrial and freshwater taxa. Taxa represented by the presence of the Lyrodusis assemblage (Holyoak et al., 1983), including Retinella (Lyrodusis) elephanthum, Rethenica filograna, Laminifera pauli, Pomatias elegans and Platyla polita were abundant in Unit C, with the occurrences of Platyla polita and Pomatias elegans also recorded in Unit B. In addition, Unit C also yielded a small mammalian assemblage, including the remains of Meles meles, Myodes glareolus, Microtus subterraneus, Arvicola terrestis cantiana and Apodemus spp. (Table 1; Wiggs, 1943; Kerney, 1959; Holyoak et al., 1983).

Kerney (1959) first suggested a Hoxnian Interglacial age for the Hitchin tufa on the basis of its stratigraphic position between two deposits of glacial origin. This attribution has since been confirmed through correlation with the Beeches Pit tufa (Bed 4, cf. Icklingham Tufa Bed), based on the occurrence of the Lyrodusis assemblage in both sequences, suggesting that they accumulated during the same temperate interval of MIS 11 (Preece et al., 2007). A further line of biostratigraphical evidence is provided by the presence of the water vole morphotype Arvicola terrestis cantiana, which only occurs in sequences in Britain from the later Cromerian Complex (MIS 13) onwards, and the pine vole, M. subterraneus, the last recorded appearance of which in the British fossil record is during MIS 11 (Schreve, 1997, 2001a).

**Methodology**

**Site excavation and sedimentology**

In 2013, an auger transect was undertaken along the length of Oughtonhead Lane (220 m), supplemented by three 1 m² test pits at intervals along the transect, in order to locate potential areas of interest near Kerney’s original site. Due to the limitations imposed by the SSSI and agricultural activity in the fields along Oughtonhead Lane, it was not possible to auger or trial pit in localities north and south of the transect line (Fig. 2).

A 2 m² excavation pit (H13-TP2) was dug in order to expose the full tufa sequence. The sequence was described following standard sedimentological descriptive terminology (Jones et al., 1999). The western face of the excavation pit was subsampled using overlapping 50 × 10 × 10 cm stainless steel monolith tins. Further micromorphological samples were extracted from the monolith tins and a total of eight micromorphological samples were prepared using standard impregnation techniques developed at the Centre for Micromorphology at Royal Holloway, University of London (Palmer et al., 2008). Thin sections were analysed using an Olympus BX-50 microscope with magnifications from 20x to 200x and photomicrographs were captured with a Pixera Penguin 600es camera.

Bulk sedimentological analyses were conducted on samples 1 cm thick taken at 2 cm intervals throughout the tufa sequence. These samples were air-dried and sieved at 2 mm and, prior to gently powdering the sample, shell fragments and ostracod valves were picked out of the samples using tweezers under a Motic Stereo Zoom Microscope. Mass specific magnetic susceptibility (MS) was measured on the <2 mm size fraction at low frequency (0.46 kHz, μ0) using a Bartington MS2 meter with dual frequency sensor following the protocol of Dearing (1999). Values are expressed as x10⁻³ m²kg⁻¹. Total organic carbon (TOC) was determined using the titration method (Walkley and Black, 1934) and calcium carbonate (%CaCO₃) content determined using a Bascomb Calcimeter (Gale and Hoare, 1991). Particle size analysis was undertaken via the laser diffraction method using a Mastersizer 2000 and Hydro MU accessory. Samples for particle size analysis were pretreated to remove CaCO₃ and organic matter using 10% hydrochloric acid and 10% hydrogen peroxide, respectively. Samples were then immersed in 0.5% sodium hexametaphosphate for 24 h to avoid coagulation. Prior to measurement, samples were subject to ultrasound for 20 min.

**Stable isotopes and trace elements**

Prior to geochemical analysis, the Hitchin tufa was screened for diagenetic alteration. Although relatively impure, the tufa sequence is composed of predominantly microbial micritic fabrics with no evidence of spar mosaic cements or diagenetic recrystallisation suggestive of substantial diagenetic alteration (e.g. Rainey and Jones, 2007). Where micropore growth has occurred around pores or rims of peloids, it does not constitute a significant volume of carbonate. Furthermore, the tufa fabric is non-luminescent under cathodoluminescence (Andrews, pers. comm.), suggesting negligible diagenetic alteration (e.g. Stone et al., 2010). Where spar is present, it is typically associated with stromatolitic fabrics, of which it has been suggested that spar crystals are the primary fabric (Brasier et al., 2011), and calcified cyanobacteria remains, with which primary spar formation has been associated (e.g. Freyetet and Verrechia, 1999). Consequently, we propose that the stable isotope and trace element records from the Hitchin sequence are unaltered and record environmental conditions that existed at the time of carbonate precipitation.

Subsamples 0.5 cm thick for stable isotope analysis (δ¹³C and δ¹⁸O) were taken throughout the tufaceous unit. To negate the effects of detrital contamination from mineral grains and biogenic carbonate material (Leng and Marshall, 2004), all samples were wet-sieved at 63 μm with Ultrapure water. Sieved samples were treated overnight with 10% hydrogen peroxide to remove organic material. All samples were then left to dry, powdered and then weighed using a Mettler Toledo XP6 microbalance. The δ¹³C and δ¹⁸O values of each sample were determined by analysing CO₂ liberated from the reaction of the sample with phosphoric acid at 90°C using a VG PRISMS series 2 mass spectrometer in the Earth Sciences Department at Royal Holloway, Internal (RHBNC) and external (NBS19, LSVCE) standards were run every four and 18 samples, respectively. All isotope data presented in this study are...
Table 1. Summary of description of Hitchin tufa by Kerney (1959). Taxa attributed to the *Lyrodiscus* assemblage based on Holyoak et al. (1983).

| Unit | Depth (m) | Sediment description | Molluscan assemblage | Vertebrate assemblage | Interpretation |
|------|-----------|----------------------|----------------------|-----------------------|----------------|
| D    | 0–0.5     | Soil: coarse, extremely ill-graded flint gravel in a matrix of brownish loamy sand, and containing patches of material derived from (C) below. Many glacial erratics, including much Jurassic debris. | No fossils | Modern soil horizon | Glacial meltwater gravels |
| C    | 0.5–0.8   | Calcareous tufa or travertine, very variable in texture. | Predominantly terrestrial, with seven freshwater taxa represented. Most abundant terrestrial taxa include *Platyla polita*, *Carychium tridentatum*, *Azeca goodalli*, *Discus rotundus*, *Platyla similis* and *Oxychilus celarius*. Freshwater taxa include *Valvata piscinalis*, *Bithynia tentaculata*, *Galba trunculata* and *Anisus leucostoma*. Presence of *Lyrodiscus* assemblage, including *Retinella (Lyrodiscus) elephantium*, *Ruthenica filograna*, *Laminifera pauli* and *Platyla polita*. | Meles meles, Myodes glareolus, Microtus subterraneus, Arvicola terestris cantiana, Apodemus sp | Tufa formation in a marshy pool environment in a temperate deciduous woodland |
| B    | 0.8–1.0   | Light brown highly calcareous sandy clay, with occasional flints and pellets of chalk. | Predominantly terrestrial (19 taxa) with minor freshwater component. Most abundant terrestrial forms include *Clausilia* spp., *Limax* spp., *Discus rotundatus*, *Cepaea nemoralis*. Presence of *Lyrodiscus* assemblage taxa *Platyla polita* and *Pomatias elegans*. | Int. bone fragment | Low-energy fluvial or solifluction deposit |
| A    | 1.0–c. 3.0 | Variable series of alternating fine sandy gravels with glacial erratics, and brown and grey calcareous loams, often almost flintless. | No fossils | Glacial outwash |
| c. 3.0+ | Chalk | | | Bedrock |
quoted against V-PDB. Trace elemental (Ca, Mg, Sr) analysis was undertaken on subsamples of the <63 µm tufa material. 0.1 g of sediment was dissolved in 25 ml of 10% acetic acid for 2 h. After filtration, 1 ml of caesium chloride-lanthanum buffer solution was added, and the samples were diluted to 100 ml using Ultrapure water. Ca, Mg, and Sr concentrations were measured in these solutions by Atomic Absorption Spectroscopy at Royal Holloway, University of London. Raw isotope and trace element data are presented in Supplementary Information 1.

Results

Oughtonhead Lane transect

Figure 2 summarises the stratigraphy of the auger and trial pit transect conducted at Oughtonhead Lane SSSI. A consistent sedimentary succession was identified along the valley, comprising (from the base of the stratigraphic sequence upwards: 1) chalk bedrock; 2) clast-rich, well-rounded and heavily patinated flint gravels (these occur locally in T2-8, T2-9 and HI13-TP2); 3) light reddish brown silt loam with large pebble-sized clasts of flint and chalk; and 4) organic-rich silt loam. Fine-grained carbonate-rich deposits were identified in two locations. First, very pale brown silt loam with powdery carbonate and centimetre-scale rounded carbonate nodules which are interbedded in the light reddish brown loam in T2-4. Second, fine-grained friable tufa is located in HI13-TP2 and HI13-TP3. In both locations, the tufa is capped by organic-rich silt clay, which in turn is overlain by matrix-rich sands and gravels. The base of the tufa was reached in HI13-TP2, where it directly overlies clast-rich gravels. Of the locations bearing tufa deposits, HI13-TP2 yielded the thickest deposit of tufa (0.7 m) and was selected as the location for sedimentological and geochemical investigations.

Stratigraphy

The HI13-TP2 stratigraphic sequence is described in full in Table 2 and photographs of the sequence are provided in Fig. 3. In summary, the sequence comprises five main stratigraphic units. The base of the sequence comprised well-sorted sands and gravels (Unit 1). This is overlain by friable, porous calcareous silt-clay grade tufa (Unit 2). The tufaceous unit is capped by organic-rich silt loam (Unit 3) which in turn is overlain by matrix-rich sands and gravels (Unit 4). Organic-rich silt loam representing the modern soil (Unit 5) caps the sequence.

Eight subunits (Units 2.1–2.8) are observed in Unit 2 based on variations in textural properties and abundances of biogenic and non-biogenic carbonate features. Unit 2.1 (0.0–0.09 m) forms massive, well to moderately sorted, silt-grade, impure granular carbonate with abundant coarse silt-medium sized mineral grains and rare occurrences of pebble-sized sub-angular flint and chalk clasts. Throughout the unit are rare occurrences of shell fragments and particulate organic material, and iron mottling is visible. Unit 2.2 (0.09–0.21 m) has similar textural properties to Unit 2.1; however, it is characterised by a lower abundance of non-carbonate mineral grains. This unit appears laterally discontinuous across the western face of HI13-TP2 where it tapers in the northeast corner of the trial pit. Unit 2.3 (0.21–0.26 m) consists of massive to normally graded silt-clay grade carbonate with frequent shell remains, including both well-preserved whole shells and shell fragments. Unit 2.4 (0.26–0.28 m) comprises pale brown silt-clay-grade carbonate with shell fragments and amorphous organic material, with a higher abundance of non-carbonate minerogenic grains relative to Unit 2.3. The unit appears discontinuous in HI13-TP2 tapering in the northeast and southwest vertices of the trial pit.

Unit 2.5 (0.28–0.35 m) is characterised by massive silt-clay-grade, low-porosity carbonate with frequent shell fragments and low abundances of non-carbonate minerogenic material. Iron staining is visible in the upper part of the stratum. Unit 2.6...
Table 2. Sediment summary and interpretation of the HI13-TP2 sequence. The Hitchin tufa is represented by Units 2.1–2.8.

| Unit | Depth (m from base of trial pit) | Description | Interpretation |
|------|----------------------------------|-------------|---------------|
| 5    | 1.55–1.88                        | Well sorted, massive dark yellowish brown (10YR 4/4) silt–sand forming moderately developed sub-angular blocky aggregates, with rootlets and medium pebble-sized chalk clasts. | Modern soil horizon |
| 4    | 0.86–1.55                        | Moderately sorted, massive matrix-rich gravels in a light reddish brown (5YR 6/4) silt–sand matrix. Gravel lithologies include flint and chalk. Isolated lenses of organic-rich material. | Moderate-energy sands and gravels either fluvial or glaciofluvial in origin |
| 3    | 0.74–0.86                        | Well sorted, massive dark brown (7.5YR 3/2) silt-clay forming well developed sub-angular blocky aggregates, with rootlets and cm-scale particulate organic material. | Soil horizon |
| 2.8  | 0.69–0.74                        | Massive, well sorted silt-clay grade yellowish brown (10YR 6/3) carbonate with fine-grained and particulate organic material throughout. Also present are rare sand-sized mineral grains and shell fragments. | Tufa |
| 2.7  | 0.39–0.69                        | Massive, highly friable silt-grade ‘blocky’ yellow (10YR 7/4) carbonate. Common occurrences of 5–15 mm spherical and sub-spherical oncoids, carbonate stem casts and shell fragments. Between 55.0 and 68.5 cm the unit is heavily iron-stained, and present are mm-scale ripples of fine-grained organic-rich carbonate. | |
| 2.6  | 0.35–0.39                        | As Unit 2.3. | |
| 2.5  | 0.28–0.35                        | Massive, very well sorted silt-clay-grade yellow (10YR 7/3) carbonate with rare occurrences of shell fragments. Mineral grains are absent. | |
| 2.4  | 0.26–0.28                        | Massive, well sorted very pale brown (10YR 7/3) carbonate with common occurrences of shell fragments, sand-granule-sized mineral grains and particulate organic material. | |
| 2.3  | 0.21–0.36                        | Normally graded, well sorted silt-grade yellow (10YR 7/3) carbonate with frequent shell remains (whole shells and fragments). Diffuse contact with: | |
| 2.2  | 0.09–0.21                        | Normally graded, well–moderately sorted yellow (2.5Y 7/4) silt-grade ‘blocky’ carbonate with abundant sand-sized mineral grains which decrease in frequency through the unit. Rare occurrences of shell fragments. | |
| 2.1  | 0.00–0.21                        | Massive, well–moderately sorted pale yellow (2.5Y 7/2) silt-grade granule carbonate with abundant sand–small pebble-sized mineral inclusions of predominantly flint, chalk and quartzite sub-angular clasts. Rare occurrences of mm–cm-scale carbonate nodules, shell fragments and amorphous particulate organic material. Iron-stained. | |
| 1    | Base of trial pit                 | Well sorted matrix-rich sub-rounded gravels in a matrix of medium–coarse sand (7.5YR 5/8). | Glaciofluvial gravels |

(0.35–0.39 m) possesses comparable textural properties to Unit 2.5 but is denser and more shell-rich than the underlying stratum. Unit 2.7 (0.29–0.69 m) is highly friable silt-grade carbonate with a high porosity and frequent spherical and sub-spherical oncoids (5–15 cm in size), phytoclasts and tufa intraclasts. The upper part of the facies is heavily iron-stained with shell fragments, and non-carbonate mineral grains are common throughout. Unit 2.8 (0.69–0.72 m) is characterised by silt-grade friable carbonate with brown silt loam with amorphous organic material forming granular aggregations. This unit forms the uppermost stratum of the tufa facies with a graded boundary to Unit 3.

**Bulk sedimentological analysis**

Unit 2 as a whole is as a predominantly silt-clay-grade carbonate (%CaCO₃ 60–90%) with occurrences of coarse silt to granule-sized non-carbonate mineral grains. Through the sequence, MS is low (-0.3 to 2.3 $10^8$ m$^3$kg$^{-1}$), and TOC is less than 1%. The TOC record exhibits minimal variation throughout the sequence; thus, it is not considered further.

Percentage CaCO₃ shows a clear pattern of variation through Units 2.1–2.8 (Fig. 4). Lower %CaCO₃ values characterise Unit 2.1 (c. 66%), with values increasing through Unit 2.2 to 73% in the upper part of the stratum. Percentage CaCO₃ is high in Unit 2.3 (80%), decreases in Unit 2.4 (75%) and subsequently rises to 90% in Unit 2.5. Percentage CaCO₃ remains high through Units 2.5–2.7, with values ranging between 80 and 90%, followed by a decrease through Unit 2.8 to 68%.

Non-carbonate minerogenic material (%siliclastic) also varies throughout the sequence (Fig. 4). High %siliclastic values are associated with lower tufa strata (Units 2.1–2.2, c. 35%) and comprises principally fine silt–fine sand-sized...
Figure 3. Photographs of HI13-TP2. (A) Photograph of HI13-TP2 logged section showing principal stratigraphic units. (B) Photograph of HI13-TP2. (C) Sketch of main stratigraphic units in Unit 2 (tufa) showing location of monolith and micromorphology samples. [Color figure can be viewed at wileyonlinelibrary.com].

Figure 4. Summary of bulk sedimentological (low-frequency mass specific magnetic susceptibility, % calcium carbonate, % siliclastic, and % sand, silt and clay of siliclastic material) properties and distribution of micromorphological features in Hitchin tufa (Unit 2). Also shown are photographs of monoliths from HI13-TP2-L1 in which samples for sedimentological, micromorphological and geochemical analyses were taken. [Color figure can be viewed at wileyonlinelibrary.com].
grains. Percentage siliclastic values decrease to 20% in Unit 2.3, increase to 30% in Unit 2.4, then subsequently decrease to between 10 and 20% in the upper tufa strata (Units 2.5–2.7). Through Units 2.3–2.7, the particle size of the non-carbonate minerogenic material is smaller than the lower tufa strata, with clay–median size grade grains predominant. An increase in siliclastic content is observed in Unit 2.8 (c. 25%) which has a generally coarser grade of sediment particle size.

Differences through the tufa strata are also observed in bulk MS (Fig. 4). High values are observable at the base of Unit 2.1 (1.55 $\times 10^{-3}$ kg$^{-1}$); MS decreases through the unit to 0.77 $\times 10^{-3}$ kg$^{-1}$ in Unit 2.2. Values continue to decrease through Units 2.3–2.5, reaching a minimum of 0.27 $\times 10^{-3}$ kg$^{-1}$ in Unit 2.5. Values remain low in Unit 2.6 (0.10 $\times 10^{-3}$ kg$^{-1}$), with average values in Unit 2.7 of 0.86 $\times 10^{-3}$ kg$^{-1}$. Evident in Unit 2.7 are distinct fluctuations in MS in the range of c. 1 $\times 10^{-3}$ kg$^{-1}$. Unit 2.8 is characterised by higher MS (1.00 $\times 10^{-3}$ kg$^{-1}$) than the underlying strata.

**Micromorphology**

At the microscale, the tufa has micritic (<4 µm) and microsparitic (5–15 µm) calcitic microfabrics with a low to moderate porosity. A range of carbonate and non-carbonate features are present, including biogenic carbonate (shell and ostracod) fragments, carbonate grains including peloids, oncoids and calcified algal and cyanobacteria remains, and stem casts (phytoclasts), and coarse silt–fine sand-sized mineral grains (Fig. 4). There is evidence throughout the sequence for syn- and post-depositional modification of the tufa fabric, with the presence of isopachous rims of micrite and microporar around pore spaces and microsparcific cement within the primary microfabrics, although this does not form a significant component of the tufa fabrics.

Unit 2.1 is characterised by a heterogeneous micritic microfabric with massive and clotted micrite, and mosaics of equant subhedral microspar crystals throughout. Well-preserved gastropod shell and ostracod valves are present, along with reworked tufa intraclasts (Figs 5A and SB). Mineral grains are abundant, many of which have evidence of peculiar alteration. Unit 2.2 is characterised by a more grain-supported microfabric comprising 2–70 µm rounded peloids of micrite and microspar with comparable carbonate and non-carbonate features present as Unit 2.1. Unit 2.3 comprises a combination of clotted micritic and peloidal microfabrics with a low porosity, rare occurrences of mineral grains and tufa intraclasts and calcified algal remains present. Unit 2.4 is characterised by a homogeneous micritic microfabric with frequent shell fragments and mineral grains. Ferruginous features are frequent in this unit; these include iron mottling of the micritic fabrics and iron overprinting of shell carbonate (Fig. 5C). Unit 2.5 is characterised by a microfabric of homogeneous, low porosity micrite with isolated crystals of equant microspar. At both the macro- and microscale, mineral inclusions are absent, although shell fragments are common. Unit 2.6 is characterised by the same macroscale and microscale properties as Unit 2.5, although an increase in shell fragments in comparison with Unit 2.5 is evident.

Unit 2.7 comprises a range of stromatolitic microfabrics, including dendroclasts and thrombolitic fabrics, which alternate with peloidal-supported and massive micritic fabrics (Figs 5D and 5E). Oncoids are common throughout the unit. At the microscale, these are characterised by concentric alternating laminations of dense massive micrite, crystalline columnar microspar and spar, and high porosity micrite and microspar. The oncoids principally possess a cortex of either clotted micrite or a void (Figs 5H and 5I). Calcified cyanobacteria filaments (Fig. 5G), and millimetre-scale phytoclasts, which occur as circular voids with a dense micritic rim and an isopachous microspar infilling are observed. Towards the top of this unit, where there is an increase in mineral grains and shell fragments, ferruginous microfabrics are present that comprise coatings around peloids, mottling within individual peloids and of the micritic fabrics, and isolated grains of siderite. Unit 2.8 is characterised by a peloidal ‘marmorised’ (Freytet and Verrechia, 2002) microfabric with a micritic cement (Fig. 5F). Ferruginous features are also present; these include aggregations of ferric spherules (10–15 µm in size) and mottled overprinting of the microfabric. An increase in the frequency of amorphous organic material is also recorded at the microscale; however, this is not recorded in the TOC content of the unit.

**Stable isotopes and trace elements**

A summary of the stable isotope and trace element data is shown in Table 3 and presented stratigraphically in Fig. 6. Measured 818O values range from -4.03‰ to -5.75‰ and measured 813C values range from -7.57‰ to -10.2‰. There is no evidence for covariation of 818O and 813C values through the sequence ($r^2 = 0.2355$, $p < 0.05$, $n = 20$).

The lowest part of the sequence (Units 2.1–2.2) is characterised by the highest 818O values, ranging from -4.03‰ to -4.48‰. The transition to Unit 2.3 is characterised by a decrease to lower 818O values, with mean values through Units 2.3–2.5 of -5.07 ± 0.38‰. Similar 818O values are also recorded throughout Unit 2.6 (mean = -4.96 ± 0.10‰), while Unit 2.7 is represented by a single sample with an 818O value of -4.24‰. Stratigraphic differences are also observable in the 813C values. Units 2.1–2.2 are characterised by 813C values ranging from -8.15‰ to -7.57‰, above which a trend of decreasing values is observable between Unit 2.3 and Unit 2.6, with values ranging from -8.06‰ to -10.20‰. Unit 2.7 is characterised by 813C values ranging from -9.68‰ to -10.10‰ and Unit 2.8, represented by one sample, has a 813C value of -7.82‰.

Measured concentrations of Mg and Sr range from 327 and 529 ppm to 56 and 104 ppm, respectively. Correlation of Mg and Sr concentration values shows no significant linear relationship ($r^2 = 0.28$, $p > 0.05$, $n = 36$), indicating that leaching of Mg and Sr from siliclastic material was negligible during acid digestion (Garnett et al., 2004). Mg/Ca and Sr/Ca molar ratios are plotted in stratigraphic order in Fig. 5. Although there is a high degree of scatter associated with the Mg/Ca and Sr/Ca ratio datasets, both profiles have a similar pattern of variation. These are summarised as: 1) relatively higher Mg/Ca and Sr/Ca values associated with Units 2.1 and 2.2; 2) a decrease to relatively lower Sr/Ca ratios in Units 2.3–2.5 while Mg/Ca ratios increase; 3) relatively stable Mg/Ca and Sr/Ca values through Units 2.6 and 2.7; and 4) a subsequent increase in Mg/Ca and Sr/Ca ratios in the upper part of Unit 2.7 and Unit 2.8.

**Interpretation**

Oughtonhead Lane stratigraphy and geomorphological context

The stratigraphic sequence at Oughtonhead Lane shows a broadly consistent succession along the southern flank of the Oughton Valley. This sequence is comparable to superficial deposits described elsewhere in the Hitchin valley (Hopson et al., 1996). Directly overlying the chalk bedrock, the clast-rich gravels represent moderate-energy glaciofluvial deposits.
associated with the infilling of the Hitchin Channel during MIS 12 (Hopson et al., 1996). In most localities, these gravels are directly overlain by light reddish brown silt loam. The lithological characteristics of this are consistent with the ‘brickearth’ deposits which are widespread in the Hitchin area, suggested to represent a combination of aeolian and soliflucted sediment deposited in cooler conditions (Reid, 1897; Kerney, 1959; Hopson et al., 1996). The organic-rich silty loam which caps these deposits represents the recent soil. The carbonate-rich very pale brown silt loam, which occurs interbedded with the brickearth deposits in T2–4 (Fig. 2), are interpreted on the basis of macroscale field observations to reflect carbonate precipitation in a shallow–water environment, possibly associated with a shallow depression in the brickearth deposits. These deposits have no clear stratigraphic relationship with the tufa deposits in HI13–TP2 and HI13–TP3 (Fig. 2) and given their stratigraphic position within the brickearth, likely formed subsequent to tufa formation in the Oughton Valley.

A broadly similar stratigraphic sequence to the rest of the Oughton Valley is identifiable in HI13–TP2. Here, Unit 1 is interpreted to reflect the lateral continuation of the Hitchin Channel glaciofluvial deposits, while Unit 4 represents a facies of the brickearth deposit. Tufa deposits (Unit 2) are found overlying the glaciofluvial deposits. These deposits are relatively thin and have a limited west–east lateral extent, possibly indicating that the tufa systems forming these deposits were relatively localised within the Oughton Valley. Land surface processes resulting in the erosion of the tufa may have also had strong control over the present distribution of the deposit (Arenas et al., 2010). This was likely to be significant in the vicinity of the Oughton Valley, given its position in relation to postulated ice margins during Middle Pleistocene glacial.

Table 3. Summary of Hitchin tufa stable isotopes (δ¹⁸O and δ¹³C) and trace element (Mg, Ca, and Sr) values

|                | N | Mean   | 1σ | Min.  | Max.  |
|----------------|---|--------|----|-------|-------|
| δ¹⁸O (V-PDB)   | 20 | -4.80  | 0.41| -5.75 | -4.03 |
| δ¹³C (V-PDB)   | 20 | -9.03  | 0.78| -10.20| -7.57 |
| Mg/Ca (10⁻³)   | 37 | 1.37   | 0.13| 1.01  | 1.54  |
| Sr/Ca (10⁻³)   | 37 | 2.37   | 0.29| 2.84  | 3.05  |
periods (Gibbard and Clark, 2011; Lee et al., 2011). The organic silt-clay (Unit 3), which caps the tufa deposit in HI13-TP2 and HI13-TP3 represents soil formation subsequent to tufa development. Given the uncertainty in the erosive history of the tufa deposit subsequent to its formation, it is unclear how the timing of soil development relates to tufa formation.

**Mode of tufa development**

The macroscale and microscale properties of the Hitchin tufa deposit are consistent with the formation of an ambient temperature freshwater tufa (Pedley, 1990; Ford and Pedley, 1996; Pentecost, 2005). Given the lateral extent and position of the tufa in the Oughton Valley, it is likely that the tufa represents a perched springline tufa deposit (following the classification of Pedley, 1990). However, it is important to note that alongside likely erosion of the tufa deposits (as described above), denudation of the Oughton Valley subsequent to MIS 11 would have acted to alter the relative topographic position of the tufa deposit in relation to the River Oughton stream channel. Variations in tufa facies through the sequence reflect changes in the relative position and flow regime of the spring (Pedley, 1990; Pedley et al., 2003; Pentecost, 2005).

Unit 2.1 represents the earliest persevered instance of authigenic carbonate precipitation. A high allochthonous input is reflected in the presence of tufa intraclasts and non-carbonate mineral grains likely transported by colluvial action (Pedley, 1990; Ford and Pedley, 1996; Glover and Robertson, 2003). The facies can be classified as a tufa based on its concretionary microfabric (Pentecost, 2005). A high allochthonous component is consistent with the development of lithoclastic tufa facies (Ford and Pedley, 1996). The lithological properties of Unit 2.2 are also consistent with lithoclastic tufa facies; however, a decrease in the frequency of non-carbonate mineral grains and tufa intraclasts observed through this unit indicate a reduction in allochthonous inputs.

The presence of peloidal and clotted micritic microfabrics within Unit 2.3, allied with a low abundance of non-carbonate mineral grains, are consistent with the development of a typical microdetrital tufa facies associated with microbially induced carbonate precipitation (Pedley, 1990, 2000; Riding, 2000; Pedley and Rogerson, 2010). The presence of microscale iron aggregates and increase in both non-carbonate mineral grains and shell fragments within Unit 2.4 are consistent with the return to the development of a lithoclastic tufa fabric (Pedley, 1990) with translocation of iron and manganese oxides occurring as a consequence of water level variations (Freytet, 1973; Alonso-Zarza and Wright, 2010). The lithological properties of Units 2.5 and 2.6 are comparable to Unit 2.3, indicating a shift back to microdetrital tufa formation.

Another shift in the style of tufa sedimentation occurs in Unit 2.7, with the presence of oncocids, tufa intraclasts and stromatolitic microfabrics consistent with oncocid tufa facies (Pedley, 1990; Ford and Pedley, 1996). The range of tufa fabrics in this unit are characteristic of in situ cyanobacterial activity resulting in carbonate precipitation, with differences in texture related to the degree and rate of calcification within the tufa system at this time (Ferris et al., 1997; Kano et al., 2003; Andrews and Brasier, 2005). The microfabrics present in Unit 2.8 are also characteristic of oncocid tufa facies. The macro- and microscale ferruginous features in this unit indicate translocation of iron and manganese oxides resulting from the fluctuation of the water table and development of the overlying soil after the cessation of tufa formation.

The association of the lithoclastic, microdetrital and oncocid tufa fabrics and abundance of non-carbonate material in the Hitchin sequence are consistent with tufa deposits associated with perched springline tufas

**Figure 6.** δ¹⁸O, δ¹³C, Mg/Ca and Sr/Ca profiles of HI13-TP2-L1. Error bars for δ¹⁸O and δ¹³C represent 1σ measurement uncertainty. Error bars for Mg/Ca and Sr/Ca represent calculated 1σ confidence interval of ratios based on 1σ measurement uncertainty of Ca, Mg and Sr. [Color figure can be viewed at wileyonlinelibrary.com].

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(Pedley, 1990; Ford and Pedley, 1996; Pedley et al., 2003; Capezzuoli et al., 2014). The variation between lithoclastic, microdetrital and oncoidal facies are indicative of a varying flow regime downstream of the spring resurgence point. Broadly, three main phases of flow regime are clear (Table 4). The lithoclastic facies that characterise the lower facies of the sequence are representative of the onset of tufa formation at the locality as a result of sheet-like flow across the former land surface redepoting reworked tufa fragments from closer to the spring resurgence point (Capezzuoli et al., 2010). A shift to more microdetrital tufa formation associated with Units 2.3–2.6 indicates formation of a low-energy, shallow-water, paludal-type environment likely in an area of impeded drainage on the valley sides. Fluctuations in water level associated with this pool environment are recorded in these strata, with Unit 2.4 representing a reduction in water level and accumulation of allochthonous material. The oncoidal facies that characterise the upper tufa strata indicate a shift to a relatively higher flow, fluvial-style flow regime (Pedley, 1990; Pedley et al., 2003). In the case of Hitchin, these strata may have formed as a consequence of increased spring activity but also may be associated with a change in the position of the main distributary channel of the spring upslope (Pedley et al., 2003). Cessation of tufa formation at the site may have been a consequence of reduced spring activity associated with a lowering of the water table or shift in spring focal point away from this locale.

Stable isotopes and trace elements

The δ18O and δ13C values of the Hitchin tufa are consistent with those recorded from modern riverine tufas and freshwater microbial carbonates from northwest Europe (Andrews et al., 1993, 1997; Andrews, 2006). Both δ18O and δ13C values are significantly lower than the range for marine limestones (Pearce et al., 2003; Leng and Marshall, 2004; Andrews, 2006; Tye et al., 2016) indicating that detrital contamination from geological carbonates had minimal impact on the Hitchin tufa isotopic signal.

Several studies of modern tufas in Britain have shown that the δ13C values of tufa carbonate are strongly related to the isotopic values of meteoric water, which in temperate mid-latitude regions reflects mean annual air temperature (Andrews et al., 1993, 1997; Darling et al., 2003; Garnett et al., 2004). Empirical studies have shown that this relationship is in the range of +0.58‰/°C (Rozanski et al., 1992, 1993; Andrews, 2006). A further temperature control is exerted on δ18O values at the time of carbonate precipitation, explained by Craig’s thermodynamic equation as -0.24‰/°C (Craig and Gordon, 1965; Hays and Grossman, 1991; Kim and O’Neill, 1997). This effectively acts to ‘dampen’ the air temperature effects on water isotopic composition, meaning that the relationship between prevailing temperatures and δ18O values of tufa carbonate at the time of precipitation will be in the order of +0.3‰/°C. Two processes can act to modify tufa δ18O: first, degassing near the spring resurgence point; and second, evaporation in standing or slow-moving water. Both processes act to increase δ18O values and cause significant covariation with δ13C (Andrews, 2006). Degassing and evaporative effects have the greatest impact in semi-arid and desert regions (e.g. Smith et al., 2004); however, they can also impart some effect on shallow water bodies with long residence times in lowland temperate environments (Andrews, 2006).

If variations in the Hitchin δ18O profile are explained solely by air temperature changes, then two trends are observable. First, relatively higher temperatures associated with the lower tufa strata (Units 2.1–2.2), and second, relatively lower temperatures associated with the upper tufa strata (Units 2.3–2.8). In both parts of the sequence, minimal changes in the δ18O values indicate low variability in air temperature throughout the interval of tufa formation. The difference in mean δ18O values between Units 2.2 and 2.3 suggests a decrease in temperature of around 2°C. It is important to note that this shift in isotope values does occur in association with the change in tufa fabric. Higher δ18O values associated the lithoclastic tufa facies in the lower strata may therefore represent some evaporative modification of the δ18O signal prior to the development of the shallow-pool environment within the perched springline tufa system (Andrews et al., 1993, 1997). The development of the tufa system with paludal and fluvial-type environments at Hitchin corresponds to a shift to more stable δ18O values in the upper strata. These values are consistent with temperate tufas with low water residence times and minimal evaporative modification (Andrews et al., 1993, 1997; Garnett et al., 2004) and thus their isotopic values more faithfully reflect prevailing air temperatures at the time of tufa formation.

Variations in δ13C values of tufa carbonate reflect relative contributions of: 1) CO2 derived from decomposition of soil organic matter (Cerling et al., 1989; Cerling and Quade, 1993); 2) geological carbon derived from the dissolution of marine limestone in the aquifer (Hudson, 1977); and 3) the dissolved inorganic carbon (DIC) load of the water from which the tufa precipitates. In tufa systems, the δ13C signature of DIC can be modified through the equilibration of the aquifer and spring water with atmospheric CO2 (Usdowski et al., 1979; Dandurand et al., 1982). In modern lowland temperate tufa systems in

Table 4. Summary of main tufa facies and inferred environmental conditions in the Hitchin tufa sequence. Also shown is inferred correlation with the tufa sequence described by Kerney (1959).

| Unit | Depositional environment | Tufa facies | Tufa environment | Temperature | Rainfall | Kerney (1959) correlation |
|------|--------------------------|-------------|------------------|-------------|---------|--------------------------|
| 1    | Glaciofluvial             | -           | -                | Cool        | A       |                          |
| 2.1  | Tufa                       | Oncoidal    | Fluvial           | Temperate   | Drier   | C                        |
| 2.2  | Lithoclastic              | Microdetrital| Pool             | Wetter      | Increasing | C (carbonaceous seam) |
| 2.3  | Microlithoclastic         | Sheet-flow  | Temperate*        | Drier       | B       |
| 2.4  | Tufa (perched springline) | Microdetrital| -                | Cool        | A       |
| 2.5  | Tufa                       | Microdetrital| -                | Cool        | A       |
| 2.6  | Tufa                       | Oncoidal    | Fluvial           | Temperate   | Drier   | C                        |
| 2.7  | Tufa                       | Microdetrital| Pool             | Wetter      | Increasing | C (carbonaceous seam) |
| 2.8  | Tufa                       | Microdetrital| Sheet-flow       | Temperate   | Drier   | B                        |

*δ18O values in this interval may in part reflect evaporative effects.
northwest Europe, δ¹³C values typically range between -8‰ and -12‰ (Andrews, 2006); the range of δ¹³C values from the Hitchin tufa are consistent with these. This indicates that DIC in the spring water feeding the Hitchin tufa is primarily a reflection of carbon sources from soil zone CO₂ derived from vegetation with a C3 photosynthetic pathway, and the effect of CO₂ degassing and equilibration with atmospheric CO₂ (both of which results in high δ¹³C values) was negligible.

One of the key features of the Hitchin tufa δ¹³C profile is the depletion trend observable through Units 2.1–2.6. Geochemical studies of tufa systems have demonstrated that the depletion in the δ¹³C signal may be a consequence of variation in the in-aquifer residence time of water prior to spring emergence (Garnett et al., 2004; Dabkowski et al., 2012). Periods of drier conditions encourage several in-aquifer processes: 1) increased exchange between atmospheric CO₂ and water in the unsaturated zone; 2) CO₂ degassing in the unsaturated zone, resulting in carbonate precipitation prior to spring emergence; and 3) increased residence time of water in the aquifer, thereby leading to increased dissolution of limestone bedrock (Fairchild et al., 2000; Ihlenfeld et al., 2003; Garnett et al., 2004; Dabkowski et al., 2012). These processes act to increase the δ¹³C values of water prior to spring emergence, and as such increase δ¹³C values of DIC. During periods of wetter conditions, these processes are reduced; consequently δ¹³C values will tend to be lower. Therefore, the depletion trend observed in the δ¹³C record through Units 2.1–2.6 may reflect a shift to wetter conditions. The upper part of the Hitchin tufa (Unit 2.7) is characterised by low δ¹³C values, suggesting stable and wetter conditions, resulting in a lower in-aquifer residence time and a higher spring flow rate. This is supported sedimentologically, with evidence for a shift to oncoidal tufa fabrics in this stratigraphic interval, characterised by the presence of oncoids, tufa intracrystals and stromatolitic microfabrics that are consistent with a higher spring flow regime.

Changes in in-aquifer residence times have also been demonstrated to control Mg/Ca and Sr/Ca ratios in temperate tufa systems (Ihlenfeld et al., 2003; Garnett et al., 2004; Dabkowski et al., 2012), with ratios principally a function of: 1) dissolution of carbonate relative to dolomite from the bedrock during the percolation of groundwater (Chou et al., 1989; Fairchild et al., 2000); 2) selective leaching of Mg and Sr in relation to Ca from limestone bedrock after Ca saturation of the groundwater is reached; and 3) prior-calcite precipitation in the aquifer before spring emergence, leading to a decrease in Ca relative to Mg and Sr (Fairchild et al., 2000; 2006). These three processes occur more readily under long aquifer residence times, and thus drier conditions, leading to higher Mg/Ca and Sr/Ca ratios in relation to wetter intervals. As described above, higher δ¹³C values of tufa are also favoured by high in-aquifer residence time (and thus drier conditions). Therefore it should be expected that through a tufa sequence, congruent shifts in Mg/Ca, Sr/Ca and δ¹³C values should be observed, if reflecting changes in palaeo-rainfall.

Although there is some variability in the Hitchin Mg/Ca and Sr/Ca profiles, broad similarities with the δ¹³C profile exist. Most evident are the higher Mg/Ca, Sr/Ca and δ¹³C values associated with the lower strata and a decrease to relatively stable lower Mg/Ca, Sr/Ca and δ¹³C values associated with the upper strata. This can be interpreted as reflecting a change from drier conditions at the base of the sequence to wetter and more stable conditions associated with the deposition of the upper strata of the Hitchin tufa. This pattern is supported by sedimentological evidence, with a shift from a paludal to fluvial-style flow regime within the tufa system. Decoupling of the Mg/Ca ratio from Sr/Ca is evident in the latter part of Unit 2.2 and extends through Units 2.3 and 2.4. Within this interval, there is sedimentological evidence for fluctuating water levels and rate of tufa deposition within the systems. These fluctuations would potentially affect the uptake of Mg²⁺ and Sr²⁺, which is controlled by precipitation rate (Tesoriero and Pankow, 1996; Dissard et al., 2010) and chemoselective processes (Rogerson et al., 2010) during tufa formation, resulting in the divergence in the records observed. Notwithstanding these differences, comparable broad trends in the datasets suggest that changes in in-aquifer residence time, and thus changes in rainfall, are reflected in the geochemical records.

**Discussion**

**Re-evaluation of the Hitchin sequence**

Evident in the HI13–TP2 sequence are broad similarities with the previously described tufa sequence in the Oughton Valley (Wiggs, 1943; Kerney, 1959). Together, both Units 2.1 and Unit 2.2 equate to Unit B as described by Kerney (1959), while Units 2.3–2.8 equate to Unit C. The ‘carbonaceous seam’ within Unit C identified by Kerney (1959) is represented by Unit 2.4 in our study (Table 4). Overall, our data support the previous interpretations of site formation proposed by Kerney (1959) and can further refine the previously proposed mode of sediment accumulation at the site. The lower strata (Unit B/Units 2.1–2.2) were classified by Kerney (1959) as brickearth deposits forming due to low-energy colluvial activity. Our data suggest that, while these strata do have a significant colluvial component, the presence of concretionary tufa microfabrics indicates that these represent the first instance of tufa deposition at the site, albeit representing sheet-flow facies downstream of a perched springline deposit. The overlying strata were previously interpreted to represent tufa formation within a marshy shallow pool environment (Kerney, 1959). Sedimentological and micromorphological data presented here indicate a more complex mode of tufa formation, with shifts between paludal and fluvial-style facies associated with changing spring flow regimes upstream of the Hitchin locality. Indeed, Unit 2.4 represents one such interval of reduction in spring flow and increased allochthonous inputs from the valley.

Using this correlation, we can relate the broad molluscan stratigraphy presented by Kerney to the Hitchin sedimentological and geochemical records for this study. It is important to note that the molluscan evidence presented by Kerney (1959) is based on single bulk samples from Unit B and Unit C, so it is not possible to link any changes in malacological succession directly to the sedimentological and geochemical record changes through the sequence. However, evident from Kerney’s observations is that fully temperate conditions persisted for the duration of tufa formation at the Hitchin locale. The malacological evidence for warm and humid conditions is reflected in the stable isotopic data from Hitchin, which lie within the range of tufas forming in temperate environments under a climatic regime similar to the present day (Andrews et al., 1993, 1997). Significantly, the presence of taxa comprising the Lyrodiscus assemblage in both Units B and C (Kerney, 1959) allows us to correlate the Hitchin sediment and geochemical records more precisely with a specific pollen substage within the Hoxnian Interglacial. As described above, the Hitchin sequence has been previously correlated with the Beeches Pit sequence on the basis of the occurrence of ‘Lyrodiscus assemblage’ in both sequences. The Beeches Pit tufa has been correlated to a specific substage of the Hoxnian...
Interglacial by means of the malacological record. The occurrence of a Lyrodiscus assemblage at Beeches Pit coincides with the relative dominance of Discus rotundatus over its congener, D. ruderatus (Preece et al., 2007). This is comparable to the pattern observed at Barnfield Pit, Swanscombe, where D. rotundatus is the dominant taxon in the Lower Middle Gravels (LMG; Preece et al., 2007; White et al., 2013). Although terrestrial species are a rare component of the predominantly fluvial molluscan assemblages from Swanscombe, the Lyrodiscus assemblage taxon Platylyta polita has been recorded in the LMG at the adjacent site of Dierden’s Pit, which lies within the same terrace (White et al., 2013). Critically, the Swanscombe sequence has now been more precisely correlated with the Hoxnian Interglacial pollen stratigraphy at Clacton-on-Sea on the basis of the presence of the ‘Rhenish’ suite of freshwater molluscs, which indicates deposition of the LMG during Hollia–b (White et al., 2013). Consequently, the formation of the tufas preserved at Beeches Pit and Hitchin can be confidently placed within Hollia–b, the climatic optimum of MIS 11c. Using this chronological framework, we can use the geochemical records from Hitchin to make inferences about the climate regime of the thermal maximum of MIS 11c in Britain.

**Temperature and rainfall regimes of the climatic optimum of MIS 11c**

The correlation of the Hitchin tufa sequence, by means of molluscan biostratigraphy, to Hollia of the Hoxnian Interglacial means that these sediments record the climatic optimum of MIS 11c in Britain. It is important to highlight, however, that it is not possible to determine exactly how much of the Hitchin tufa record, due to uncertainty associated with determining the duration of Hollia (Candy et al., 2014) and the highly variable rate of tufa carbonate precipitation in temperate environments (Pentecost, 2005; Capezzuoli et al., 2014).

The δ18O profile from the upper strata at Hitchin is interpreted to reflect changes in temperature at the time of tufa deposition. The consistency in δ18O values observed in the upper strata at Hitchin indicates minimal variation in temperature within part of Hollia, with values representing warm and stable thermal conditions throughout the interval of tufa formation. The only other δ18O record of the Hoxnian Interglacial is from the lacustrine sequence at Marks Tey (Tye et al., 2016). Here, the δ18O record indicates the persistence of stable temperatures during Hol–Holl (the exception being the decrease in temperatures in association with the non-arboreal pollen phase during Hollc). The δ18O values from strata correled to Hollia indicate that Ho Illa–b was characterised by higher temperatures than Holl (HOⅤ) is not recorded in the part of the Marks Tey sequence analysed by Tye et al., 2016). However, the Holl sediments at Marks Tey were brecciated, thus, while they yield information about the general isotopic characteristics of this interval, they lack stratigraphic integrity (Tye et al., 2016). The Hitchin stable isotope dataset indicates that the stable thermal regime that characterised Hol–II also persisted for at least part of late temperate phase of the Hoxnian Interglacial, Holl. Together, both the Hitchin and Marks Tey isotope records provide compelling evidence to indicate that, in Britain, a large part of MIS 11c was characterised by long-term thermal stability.

Variations in the sedimentology, δ13C profile and trace elements of the Hitchin tufa indicate changing hydrological conditions during Holl. Together these records exhibit a decrease from longer to shorter in-aquifer residence times of spring water prior to tufa formation accompanied by a transition to a higher energy, spring flow regime. Assuming rainfall is the principal control on in-aquifer residence times, these changes can be interpreted as a shift to relatively enhanced rainfall during Holl, and potentially then a reduction in rainfall associated with the cessation of tufa formation at the site. The occurrence of humid conditions during tufa precipitation at Hitchin is supported by the presence of several central European forest land mollusc species, many of which are included in the Lyrodiscus assemblage, and species such as Perforatella subrufescens and Leioystyla anglica, which indicate a wetter climate than prevails today in southern Britain (Rousseau et al., 1992; Preece et al., 2007).

Data from Hitchin provide the first geochemical record of changing palaeorainfall in Britain during MIS 11c. This adds to evidence previously based on sedimentological evidence in several Hoxnian lake sequences (Turner, 1970; Gibbard, 1977; Gibbard and Aalto, 1977; Gibbard et al., 1986; Boreham and Gibbard, 1995; Ashton et al., 2008). Sedimentary hiatuses at these sites are considered to reflect changing water levels and are linked to changes in either the amount or seasonality of rainfall. Generally, a rise in lake level is recorded at the end of Holl, followed by a later rise at the start of Holla (Gibbard and Aalto, 1977; Gibbard et al., 1986; Boreham and Gibbard, 1995). A reduction in lake level is also recorded at several of these sites during the Hollb–IV transition (Turner, 1970; Ashton et al., 2008). The timings of these changes agree well with the evidence for changing rainfall in the Hitchin record, indicating that these variations are probably reflecting regional shifts in rainfall during this period.

The Hitchin record can also be placed in the context of MIS 11c climates in northwest Europe through comparison with the geochemical profile from the La Celle tufa sequence (Dabkowski et al., 2012; Fig. 7), although the greater spatial distance between Hitchin and La Celle, as opposed to Hitchin and other British Hoxnian sites, makes such comparisons more speculative. The two sequences are correlated on the basis of the occurrence of Lyrodiscus assemblage taxa in both sequences (Limonid-Lozouet et al., 2006; Limonid-Lozouet and Preece, 2014; Limonid-Lozouet et al., 2020). Given the limited malacological data from Hitchin, we can only tentatively correlate tufa formation at Hitchin to the interval that the forest optimum is recorded at La Celle (Fig. 7, Mollusc zones D and/or E, Limonid-Lozouet et al., 2020) The δ18O record from La Celle indicates the occurrence of fully temperate conditions during this interval, followed by a decrease to relatively cooler conditions. The δ13C and trace element records through the same interval indicate changing palaeorainfall regimes, with principally wetter conditions associated with the thermal maximum, followed by a decrease in humidity. It may be that tufa formation during Holl at Hitchin corresponds to maximum temperatures and enhanced humidity during Mollusc zone D at La Celle, with drier conditions and a cessation of tufa formation at Hitchin related to the onset of the more open forested environments and less temperate conditions recorded at La Celle (Mollusc zone E). Ongoing high-resolution molluscan analysis at Hitchin will provide a clear insight into the malacological succession at Hitchin, enabling a more robust correlation with the La Celle sequence. However, these first results from Hitchin do indicate the potential of the sequence to record widespread patterns of temperature and rainfall regimes during the climatic optimum of MIS 11c.

**MIS 11c warmth in the context of Quaternary interglacials**

The isotopic data from Hitchin tufa also allow for the levels of warmth achieved during the climatic optimum to be compared...
with those of other Middle Pleistocene interglacials and the Holocene (Fig. 8). As outlined above, $\delta^{18}O$ values of temperate lowland tufa carbonates are related to fluctuating air temperatures, with higher $\delta^{18}O$ values corresponding to warmer temperatures, and lower $\delta^{18}O$ values corresponding to relatively cooler temperatures (Andrews et al., 1993, 1997; Garnett et al., 2004; Andrews, 2006). It is important to note that differences between isotope values can also be related to non-temperature factors such as changing air mass trajectory, source water and ice volume (Rozanski et al., 1992, 1993). In the MIS 11-aged sites of Hitchin, Beeches Pit and La Celle, tufa carbonate $\delta^{18}O$ values plot higher than those from modern, Holocene, MIS 5e and MIS 7c/7e tufa carbonates (Fig. 8). This suggests that tufa carbonate formation at the three sites representing at least part of MIS 11c probably took place under warmer temperatures than the present day, Holocene and MIS 7c/7e. This evidence is corroborated by biologically derived palaeotemperature estimates from several MIS 11c sequences in Britain, which show that temperatures during MIS 11c were warmer than the present day (Gibbard and Aalto, 1977; Coxon, 1985; Gibbard et al., 1986; Candy et al., 2010; Coope, 2010). The Hitchin and Marks Tey $\delta^{18}O$ values, together with $\delta^{18}O$ records from northwest European sequences (Dabkowski et al., 2012), add to the growing body of evidence from terrestrial sequences in northwest Europe (Mania et al., 1994; Limondin-Lozouet et al., 2010, 2015; Candy, 2009), which, combined with North Atlantic sea-surface temperature records (Stein et al., 2009; Rodrigues et al., 2011), suggest that MIS 11c may have been characterised by a greater level of warmth than during the Holocene.

Figure 7. Inferred correlation between Hitchin, La Celle and MIS 11 stratigraphy. Hitchin $\delta^{18}O$ and $\delta^{13}C$ profiles and inferred climatic conditions are plotted against Hoxnian Interglacial pollen stratigraphy. These profiles are correlated to the La Celle $\delta^{18}O$ and $\delta^{13}C$ records (Dabkowski et al., 2012) on the basis on the occurrence taxa of Lyrodiscus assemblage in both sequences and the tentative correlation is shown by the green dashed lines. Also shown are the climate zones (Dabkowski et al., 2012) and mollusc biozones (Limondin-Lozouet et al., 2020) for the La Celle sequence. The interval of forest maximum and the forest optimum are highlighted. MIS 11 stratigraphy is represented by EPICA Dome C δD record (Jouzel et al., 2007). Tentative correlation of the forest maximum recorded in the La Celle sequence to the thermal optimum of MIS 11c is highlighted. Alignment of the Hoxnian Interglacial pollen stratigraphy to the EPICA Dome C profile (Candy et al., 2014) is also shown. This alignment places Holloa at the same interval as the thermal optimum of MIS 11c. [Color figure can be viewed at wileyonlinelibrary.com].

Figure 8. Measured $\delta^{18}O$ and $\delta^{13}C$ of tufa carbonate from Britain and northwest Europe. Presented are mean ($\pm 1\sigma$) $\delta^{18}O$ and $\delta^{13}C$ values from Hitchin compared with mean ($\pm 1\sigma$) $\delta^{18}O$ and $\delta^{13}C$ values for modern tufa deposits in Britain (Andrews et al., 1993), Holocene tufa deposits from Wateringbury, Kent (Garnett et al., 2004), and Pleistocene tufa deposits form West Stow, Beeches Pit, (Preece et al., 2007), Marsworth (Murton et al., 2001), La Celle (Dabkowski et al., 2012) and Caours (Dabkowski et al., 2016). [Color figure can be viewed at wileyonlinelibrary.com].
Conclusions

Combined sedimentological, petrological and geochemical evidence from the Hitchin tufa provide a record of changing environments during the climatic optimum of MIS 11c in Britain. The tufa deposits at Hitchin represent part of a perched springline tufa deposit, with the principal facies representing the development of sheet-flow, paludal-style and fluvial-style facies. These are interpreted as representing variations in spring flow regime and/or position. Correlation with the Hoxnian pollen record indicates that the tufa was deposited during pollen stage HolII, the interval suggested to represent the thermal optimum of MIS 11c in Britain.

Measured δ18O values are consistent with lowland tufas formed in temperate environments. The δ18O values at the base of the sequence are interpreted to reflect a combination of temperature and evaporative processes. Stable δ13C values characterise the upper tufa strata and are interpreted as being controlled by temperature. The absence of significant shifts in δ18O values through the sequence indicate a stable temperature regime during the thermal optimum of MIS 11c. Measured δ18O values are comparable to those seen at other MIS 11c tufa sites and, for the most part, higher than those recorded for the present, the Holocene, MIS 5e and MIS 7, potentially implying that the thermal maximum of the Hoxnian was warmer than in these other time periods.

The δ13C and trace element profiles through the Hitchin tufa sequence are interpreted to be controlled by rainfall, and consequently provide the first geochemical evidence for changing rainfall patterns during MIS 11c in Britain. The data indicate that during the interval of tufa formation, there was a shift from relatively drier to wetter conditions, contemporaneous with a shift to tufa facies indicating a higher spring flow regime. These shifts correspond with lake-level evidence from other sequences in Britain and geochemical records from tufa sequences in France, potentially indicating regional changes in rainfall regimes associated with the climatic optimum of MIS 11c.

Supporting information

Additional supporting information can be found in the online version of this article.

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Data availability statement

The data that support the findings of this study are available in the online Supporting Information.

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