Lessons from Star Carr on the vulnerability of organic archaeological remains to environmental change

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Examples of wetland deposits can be found across the globe and are known for preserving organic archaeological and environmental remains that are vitally important to our understanding of past human–environment interactions. The Mesolithic site of Star Carr (Yorkshire, United Kingdom) represents one of the most influential archives of human response to the changing climate at the end of the last glacial in Northern Europe. A hallmark of the site since its discovery in 1948 has been the exceptional preservation of its organic remains. Disturbingly, recent excavations have suggested that the geochemistry of the site is no longer conducive to such remarkable survival of organic archaeological and environmental materials. Microcosm (laboratory-based) burial experiments have been undertaken, alongside analysis of artifacts excavated from the site, to assess the effect of these geochemical changes on the remaining archaeological material. By applying a suite of macroscopic and molecular analyses, we demonstrate that the geochemical changes at Star Carr are contributing to the inexorable and rapid loss of valuable archaeological and paleoenvironmental information. Our findings have global implications for other wetland sites, particularly archaeological sites preserved in situ.

organic artifacts | geochemistry | environmental change | analytical chemistry | wetland archaeology

Globally, wetland and peatland deposits are an invaluable source of archaeological information, preserving organic materials and macroremains that are rarely found elsewhere (1). However, these sites are also extremely sensitive to environmental changes, particularly to changes in the water table (2–4). Understanding how changing environmental conditions and geochemical parameters affect organic preservation in archaeological sites has become increasingly important because both human and climate-driven modifications of wetland environments continue to occur worldwide (5, 6). This understanding is particularly imperative because a strategy of preserving archaeological sites in situ (based on the principle that avoiding excavation protects the archaeology for the benefit of future researchers) has become increasingly prevalent since the advent of the Valetta Treaty (7).

The wetland site of Star Carr has yielded remarkably well-preserved organic remains, including 22 red deer antler headdresses thought to be used in shamanic rituals (8) and 97% of the Mesolithic antler barbed points found in Britain (Fig. S1) (9). The exceptional preservation of macrofossils and pollen has also allowed detailed reconstruction of the environmental context of the site (10); as such, Star Carr is an important archive of the human response to the end of the last glacial in Northern Europe. Sadly, the site also represents a lesson in the immense impact that human-driven environmental change can have on our cultural heritage: During excavations between 2006 and 2010, an alarming level of deterioration of both bone and wood was reported. Some bone samples were found demineralized (familiarly termed "jellybones"), and much of the wood excavated was flattened and extremely crumbly (Fig. 1) (11), in stark contrast to the outstanding quality of the organic remains uncovered in the initial excavations in the 1940s (12) and 1980s (13). In addition, the recently reported loss of palynological information (10) is testament to the fragility of the paleoenvironmental remains.

This accelerated deterioration has been attributed to modification of the water table at Star Carr via the insertion of a series of field drains in 2000 AD. As a result, the water table now lies below the cultural layers in parts of the site (14, 15). Organic preservation at wetland sites is achieved primarily through the suppression of aerobic microbial activity through constant waterlogging (16, 17). At Star Carr, in addition to this loss of waterlogging, high concentrations of sulfur have been identified that are thought to originate from pre-Holocene pyrite-rich Kimmeridge and Speetum marine clay deposits underlying the peats, which contain the archaeological materials (14).The combination of the introduction of oxygen to the sediments and these sulfur-rich deposits has led to oxidation of sulfides to sulfuric acid, causing sediment pH as low as 2 (14). However, robust data linking these environmental changes with the striking organic deterioration witnessed within 30 y at Star Carr were severely lacking (11), making an informed decision on the appropriate management of the site impossible. Focusing on the effects of site acidity on the macroscopic and archaeological remains, we undertook laboratory-based experiments to investigate the behavior of bone (18) and wood (19) in high concentrations of sulfuric acid. Results indicated that acidification is a major factor leading to the demineralization of bone and cellulose depletion in wood (Fig. 1).

However, acidity is unlikely to be the sole factor facilitating organic diagenesis at Star Carr. Therefore, to achieve a more realistic representation of the burial environment, we constructed three microcosms in the laboratory (20): A, containing sand; B, containing garden compost; and C, containing peat collected from the Star Carr site. Saturated, fluctuating, and dry

Significance

Wetland deposits provide a unique repository of archaeological and environmental information, preserving organic remains rarely found elsewhere. Star Carr is an impressive example, having provided unique evidence for human interactions with the landscape at the end of the last ice age. Tragically, here we provide experimental evidence that human modifications of the local environment are leading to changes in the site's geochemistry, resulting in the rapid loss of bone and wood artifacts. Our research demands a reassessment of the assumption that sites such as Star Carr should be preserved in situ for the benefit of future researchers and demonstrates that potential changes to the burial environment must be considered before such a policy is pursued.

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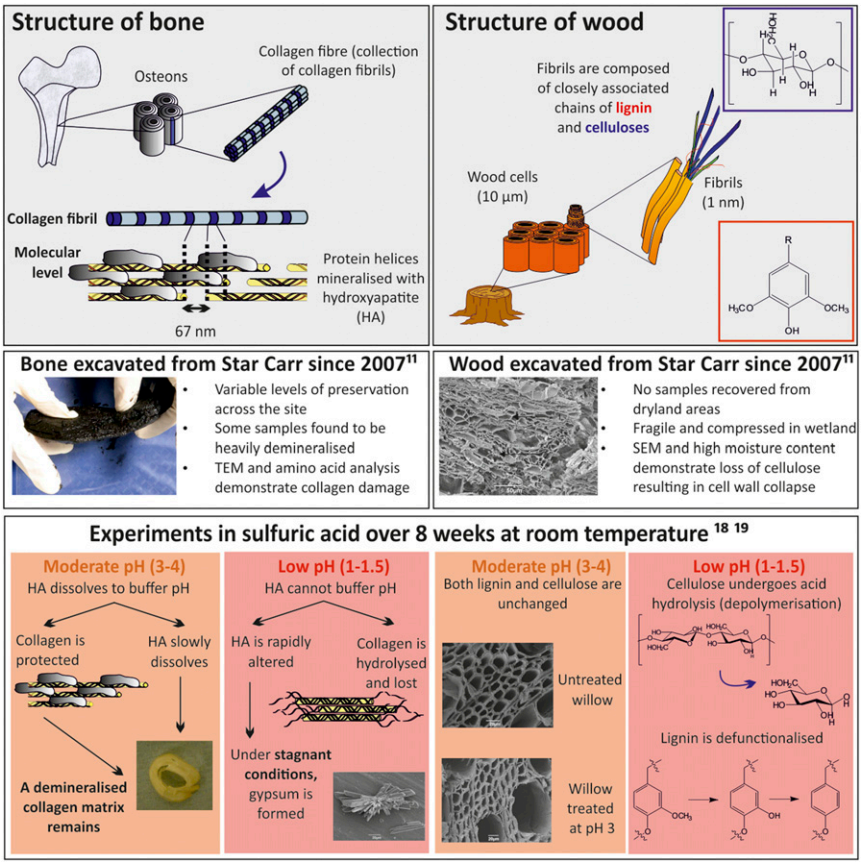
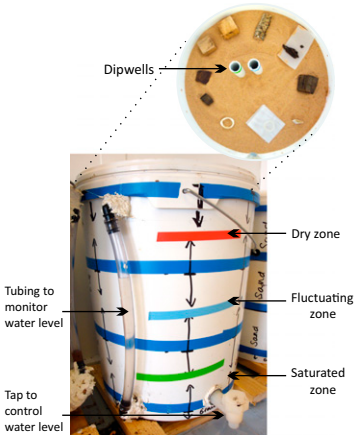


Fig. 1. Schematic of related research at Star Carr. Schematics show the basic structure of bone and wood. Observations reported following excavations at Star Carr in 2006–2010 (11) and previous laboratory-based experiments reporting changes observed in collagen and HA in bone (18) and in lignin and cellulose in wood (19) are summarized.

zones were established within each microcosm, and a range of materials was buried in each zone for 12 mo (Fig. 2).

Material was selected to enable direct comparison both with material excavated from the Star Carr site and with materials used in previously reported laboratory-based experiments in acid (Table S1) (18, 19). This material consisted of archaeological and modern wood, archaeological and modern bone, and modern sheep bone that had been demineralized by treatment in hydrochloric acid [to be comparable to the jellybones excavated from Star Carr (11)].



Zone	Sediment/ Hydrology	pH	Redox (mV)
A1	Sand/ Saturated	7.35	54
A2	Sand/ Fluctuating	7.4	173
A3	Sand/ Dry	7.26	188
B1	Compost/ Saturated	3.58	176
B2	Compost/ Fluctuating	5.58	194
B3	Compost/ Dry	5.00	435
C1	Star Carr/ Saturated	1.63	501
C2	Star Carr/ Fluctuating	1.84	559
C3	Star Carr/ Damp	1.58	571

Fig. 2. Experimental microcosms allowing assessment of sediment type and hydrological conditions on organic decay. Three microcosms were set up in 25-L fermentation buckets. A set of material was laid out in each of the 10 zones as shown. The table displays the pH and redox values for each zone recorded on excavation.

After 12 mo of burial, the level of deterioration in experimental material was compared with that in archaeological bone and wood excavated from Star Carr itself, using a suite of analytical techniques: an initial visual assessment and analysis of mass loss, followed by chiral amino acid analysis (AAR) and powder X-ray diffraction (p-XRD) for bone and Fourier transform infrared spectroscopy (FTIR) and pyrolysis gas chromatography (py-GC) for wood. Our approach has demonstrated that under the extreme geochemical conditions identified in areas of the Star Carr site, both bone and wood are at critical risk of rapid and irreversible deterioration; these findings have critical implications for any organic materials remaining in situ at the site.

Results

Geochemical Parameters Support the Validity of Microcosm Conditions. A geochemical survey carried out in 2009 recorded low pH in large parts of the Star Carr site, although localized variations were seen, appearing to correlate with the distribution of underlying pyrite-rich clay lenses (14). Further geochemical analysis carried out as part of this study concurred with the previous geochemical survey: Regions of high acidity (~pH 2) existed in close proximity to more neutral areas (Fig. S2).

To enable comparison between the microcosm experiment and the in situ burial environment, we measured pH and redox potential in each microcosm zone at the end of the experiment

(Fig. 2). Redox and pH are intrinsically linked and can provide an indication of the potential for organic remains to survive (21). Redox potentials >400 mV indicate highly oxidative sediments, which can correlate to high levels of microbial activity and, by proxy, to a low propensity for organic material to survive (20, 22).

A highly oxidative and acidic environment is demonstrated in all four zones of microcosm C (Fig. 2) and is comparable to that observed in substantial areas of Star Carr site (14). The reduced pH in zone C4 (dry) can be explained by the presence of oxygen causing increased oxidation of sulfides, which are abundant in the peat at Star Carr (14), to sulfuric acid.

In contrast, moderate pH and redox values are seen throughout microcosms A and B, with the exception of the aerated zone of microcosm B, where a redox potential >400 mV and almost neutral pH provide ideal conditions for extensive microbial colonization (20), and in the saturated zone of microcosm A, where a neutral pH and low redox potential confirm the absence of oxygen.

Rapid Loss of Hydroxyapatite Under Conditions Equivalent to Those of Star Carr. Remarkable visible transformation of all mineralized bones excavated from microcosm C was seen after only 12 mo of burial; the bones appeared swollen and lighter in color (Fig. S3), with an increased mass (Table S2). Conversely, in microcosms A and B, minimal deterioration resulted in little or no mass loss in all mineralized bone. The reverse was seen for demineralized jellybone samples: Their complete disappearance in the saturated regions of both A and B and high mass loss in the fluctuating and dry zones show that demineralized bone is lost rapidly under certain geochemical and hydrological conditions. In microcosm C, however, the jellybone samples appeared relatively intact and displayed a lower mass loss than those excavated from microcosms A and B (Table S2).

All mineralized bone samples from hydrated environments in microcosm C displayed a p-XRD pattern characteristic of gypsum (calcium sulfate) (Fig. 3) rather than the broadened hydroxyapatite (HA) peaks characteristic of unaltered bone mineral (23). We do not know of any other reports of this definitive transformation in buried bone; we hypothesize that in hydrated zones HA dissolution occurs, followed by recrystallization, incorporating sulfur from the sediments to form gypsum. Incorporation of sulfur also explains the observed mass increase and is consistent with our previous experiments carried out in sulfuric acid only (18). In contrast, the bone mineral appeared unaltered (compared with the starting material) for the samples from microcosms A and B (Fig. 3).

The minimal differences in amino acid concentration observed in most samples could be attributed to the short time scale of the experiment. However, a small reduction in total amino acid content in the archaeological bone (Star Carr rib) buried in microcosms A and B suggests loss of the protein fraction of the bone (Fig. S4). The total amino acid concentration apparently was also reduced in many of the samples from microcosm C, but mass balance indicates that this reduction is likely to be an artifact of the mass gain observed rather than indicative of protein loss.

Aspartic acid (Asx) racemization has been used as an indicator of collagen damage (24, 25). For most modern bone samples Asx racemization remained unaltered in all microcosms. However, in the archaeological bone, although variability is high, a slightly elevated Asx racemization indicates some collagen damage, with the highest values observed in microcosm C (Fig. S4). This finding concurs with the slightly reduced amino acid content also observed in microcosm C.

Chemical Degradation of Lignin Under Conditions Equivalent to Those of Star Carr. Minimal visible alteration was observed in wood samples after 12 mo. As in the bone samples, a clear mass gain was observed in many wood samples from microcosm C, indicating uptake of chemical species from the burial environment (Table S3).

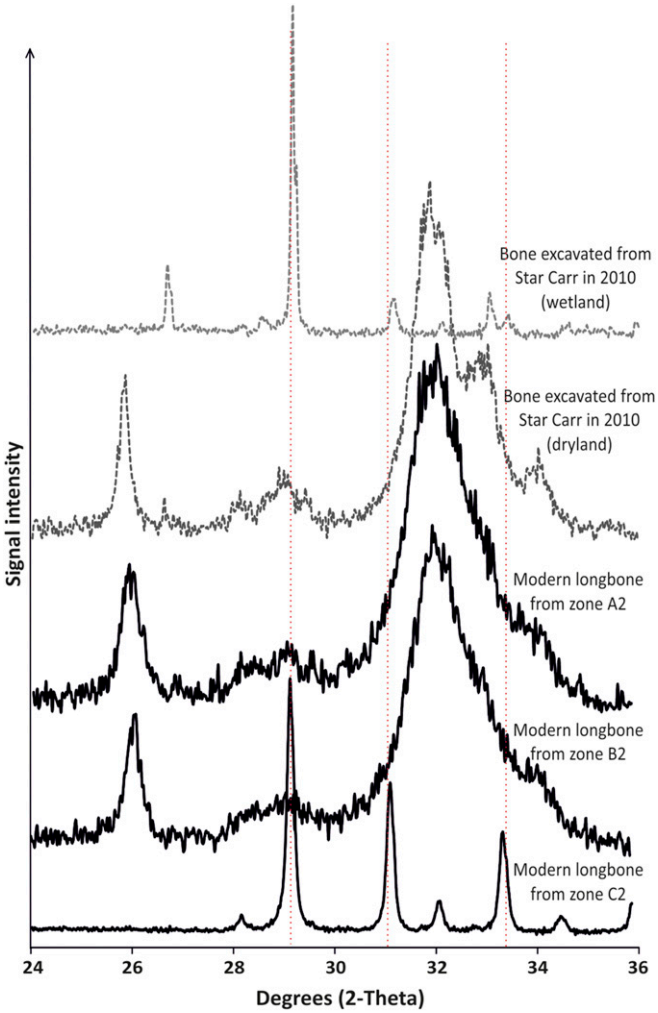


Fig. 3. p-XRD demonstrates significant alteration of HA in microcosm C. p-XRD patterns for modern long bone excavated from zone 2 (fluctuating) from microcosms C (Star Carr), B (compost), and A (sand). Although no alteration from fresh bone (characterized by broad, ill-defined peaks) is seen in modern bone from microcosms A and B, complete alteration of HA is observed in modern bone from microcosm C, with bone buried for 12 mo displaying the characteristic diffraction pattern of gypsum (indicated by dotted lines). Archaeological bone excavated from the dryland part of Star Carr in 2008 shows the dominance of HA (the slight splitting of the peak at 32 °2θ is the result of increased HA crystallinity caused by diagenesis), but material from the wetland area of the site confirms the gypsum transformation observed under microcosm experimental conditions.

Lignin defunctionalization occurred in all modern wood samples from hydrated zones of microcosm C. In the FTIR spectrum, this defunctionalization manifests as the complete disappearance of the absorbance at 1,240 cm^{-1}, characteristic of the methoxy group on lignin and therefore signifying defunctionalization of the lignin polymers (Fig. 4) (26). This finding was confirmed by increased concentrations of phenol (defunctionalized lignin) and almost complete loss of other lignin degradation products observed using py-GC (Fig. S5) (27, 28). Lignin is normally found largely intact in waterlogged archaeological samples because it is chemically stable and resistant to most forms of microbial attack (28, 29); indeed, no evidence for lignin defunctionalization was seen in samples from microcosms A or B.

The continued presence of low-intensity absorbance peaks at 1,325 and 1,375 cm^{-1} in samples from hydrated zones in microcosm C indicates that at least some cellulose remains in situ.

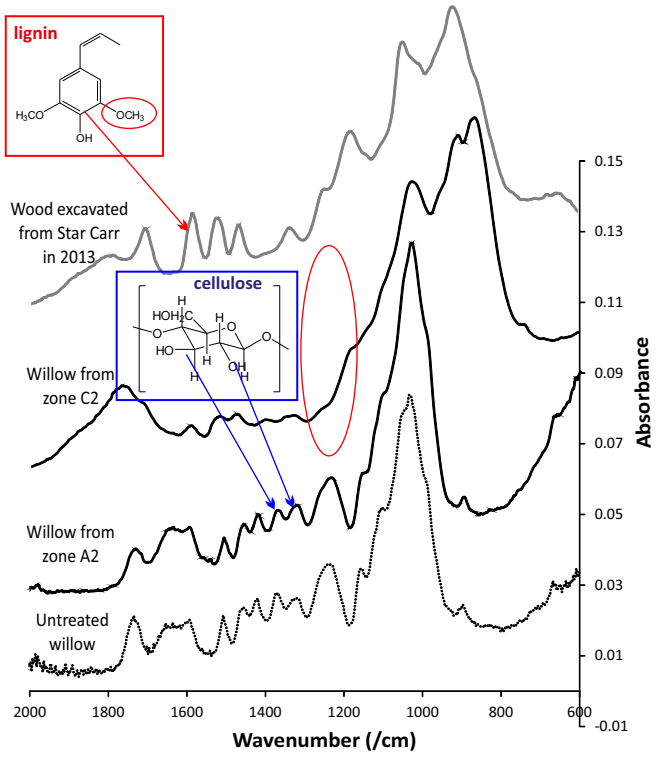


Fig. 4. FTIR analysis demonstrates defunctionalization of lignin in microcosm C. Shown are spectra from untreated willow and from willow buried in sand (A2) or in Star Carr peat (C2) for 12 mo. Loss of cellulose in the C2 sample is shown by a slight reduction in the intensity of the peaks at 1,325 and 1,375 cm^{-1} (characteristic of CH_2 groups in cellulose). Defunctionalization of lignin is indicated by the loss of the peak attributed to CH_3O groups at 1,240 cm^{-1} (circled). For comparison, a sample of wood excavated from Star Carr in 2013 is shown. Cellulose peaks remain at 1,325 and 1,375 cm^{-1}, but splitting and decreased intensity of the 1,240 cm^{-1} lignin peak indicate that lignin has become defunctionalized.

Because cellulose normally is lost far more readily through chemical hydrolysis, its survival (despite the defunctionalization of the more stable lignin) is surprising. However, analysis by py-GC showed an absence of peaks caused by cellulose, suggesting that although cellulose may have been present, it was partially degraded and therefore was lost during sample preparation for GC (Fig. S5). Analysis by both FTIR and py-GC indicated minimal chemical or biological deterioration of cellulose in samples from microcosms A and B.

Degradation in Material Excavated from Star Carr After 2007 Supports Microcosm Data. Macroscopic preservation of archaeological bone samples excavated after 2007 varied greatly across the Star Carr site. In areas of the site that had always been dryland, bone tended to be chalky and brittle; in contrast, in waterlogged parts of the site, bone was often jelly-like because of demineralization. In comparison, a single bone analyzed from the 1948 excavations was incredibly robust with very little discoloration. These differences across the site indicate differing mechanisms of diagenesis. AAR analysis confirmed these differing mechanisms: Total amino acid concentrations were very low in the chalky dryland bones (demonstrating depletion of bone protein) but were elevated in the wetland bones (indicating depletion of bone mineral) (Fig. 5). Asx racemization levels (D/Ls) were elevated in all the dryland bones, significantly exceeding the racemization reported in a rhino bone from ∼112 ka from Kirkdale (D/L = 0.13) (Fig. 5) (30) and indicating the loss of quaternary structure in any collagen still remaining (25). Conversely, many of the bones defined as jellybone display a Asx D/L value similar to that of modern untreated bone (∼0.06), signifying that the remaining collagen is relatively intact. However, it is impossible to determine how much structurally compromised collagen may have been lost after demineralization, resulting in a reduced apparent level of racemization.

Differing diagenetic mechanisms across the site are also evidenced by analysis of the bone mineral: Some samples excavated from the wetland had turned to jelly and others to gypsum. In the jellybone samples, characteristic HA peaks were completely absent from the p-XRD patterns, whereas in other bones peaks characteristic of gypsum were seen (Fig. 3). This transformation to gypsum confirmed the observations in the experimental burials and demonstrates that equivalent diagenetic processes occurred in the microcosms, indicating that these artificial environments accurately mimic in situ diagenesis.

Archaeological wood from Star Carr has been found exclusively in the wetland parts of the site; the absence of archaeological wood in other parts of the site is attributed to the rapid deterioration of archaeological wood commonly seen in non-waterlogged contexts (31, 32). Although the excavated wood was soft, it was still visually identifiable and comparable in appearance to wood excavated from other waterlogged sites of similar age (32).

Molecular analysis of samples excavated in 2013 indicates that, although cellulose had been depleted, it was not completely lost; peaks relating to cellulose were detected using both FTIR and py-GC. In addition, lignin was still present in the majority of samples, although an increased concentration of phenol and slight splitting of the FTIR peak at 1240 cm^{-1} indicate defunctionalization (Fig. 4 and Fig. S5) (26, 28).

Discussion

These microcosm experiments have highlighted the extremely rapid alterations observed in both bone and wood buried in peat from Star Carr. Although previous experiments in acid alone had shown that HA deteriorates rapidly at low pH (18), our extending the study into a more realistic representation of the burial environment at Star Carr has provided critical evidence that both bone and wood are at immediate risk at the site. Specifically, we have shown that the soil-water content is a major influence in the rapidity at which organic material is lost, consolidating a number of field-based studies (4, 33).

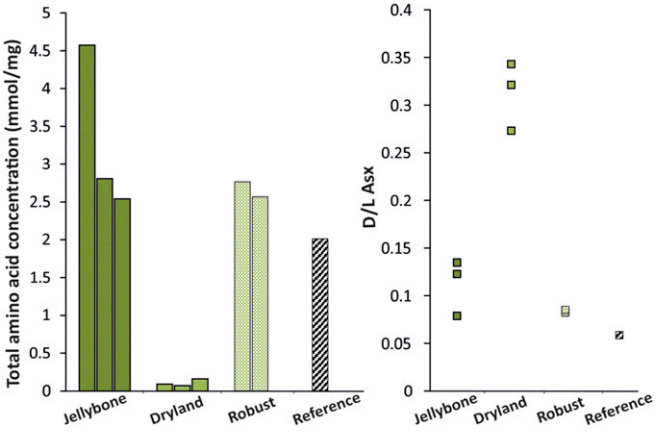


Fig. 5. Amino acid analysis shows differing mechanisms of bone degradation at Star Carr. A comparison of the total amino acid concentration (*Left*) and Asx racemization values (*Right*) for bones excavated from Star Carr in 2013 from the wetland (classified as "jellybone" or "robust") and dryland. A modern sheep bone is used as a reference. Low amino acid concentrations and high Asx racemization in the dryland bones suggest collagen damage, whereas elevated amino acid concentrations and low racemization in the wetlands indicate loss of bone mineral.

We have shown that HA dissolves rapidly under the potential conditions of low pH and high redox present in Star Carr peat (microcosm C), and, as we report here, complete transformation of the bone apatite to gypsum is observed. Critically, the short time scale of this experiment (12 mo) highlights the alarming rate at which this process can occur, raising concerns for the continued survival of bone buried at Star Carr and other archaeological sites with similar conditions. Indeed, analysis of several archaeological bones from excavations at Star Carr has shown that this process already has occurred in some areas of the site. The long-term effect of this alteration of HA on the collagen is uncertain. However, binding interactions with the mineral are vital to the survival of proteins in biominerals over long time scales (34), and HA is known to protect collagen by excluding enzymes and reactive chemical species (35). Therefore it is reasonable to assume that a change in its structure would be detrimental. Because the survival of collagen in archaeological bone is essential for the extraction of data for radiocarbon dating (36), species identification (30), and dietary isotope analysis (37), understanding the diagenetic processes affecting collagen is crucial.

Analysis of archaeological materials shows different modes of bone deterioration across Star Carr, likely to be the result of extreme variations in the geochemistry of the sediments. In the dryland areas, an HA shell is left behind after collagen depletion, and in the wetland regions the opposite occurs, leaving a collagen-rich jellybone. The formation of jellybones is almost certainly the result of the dissolution of HA to buffer acidic sediments; critically, laboratory-based experiments have shown that archaeological bone is less able to mitigate acidity via this mechanism (18) and therefore will be at greater risk in acidic sediments than modern material.

Although the degradation in archaeological wood from Star Carr was not as advanced as that in bone, extensive defunctionalization of lignin occurred in microcosm C (Star Carr peat) within only 12 mo. It is possible that this defunctionalization was biologically driven, but because lignin is normally resistant to biological decay (29, 31), a chemical mechanism is more likely.

The Star Carr sediment used in the microcosm experiments had a lower pH than has been recorded at the site itself, although geochemical analysis indicates that areas of the site remain highly acidic. Critically, these experiments have allowed an assessment of how organic materials may be affected if the site continues to change. Because the water table recently has dropped to below the archaeological zone (14, 15), the sediments bearing archaeological material are likely to continue to oxidize, becoming even more acidic. These microcosm experiments have shown that, if this further acidification occurs, bone mineral is likely to rapidly undergo a rapid transformation to gypsum, and lignin in wood is vulnerable to chemical degradation. Both processes will result in the loss of unique archaeological evidence. As such, any bone and wood artifacts left in situ at the site are at immediate risk of increased deterioration or eventual loss.

The drying out of the site also puts organic material, particularly wood, at greater risk of deterioration via biological processes. Studies have demonstrated that microbial activity is a major factor in organic deterioration (28, 38) and that biological activity is suppressed at low pH, as at Star Carr (39). There has been a lack of evidence for microbial activity in microcosm C, even where oxygen is present; however the loss of jellybone samples in the microbially rich microcosms (sand and compost) indicates that exposed collagen would be lost rapidly were biological activity feasible. The reported drying out of the sediments (14) is likely to result in increased fungal and microbial activity, possibly resulting in the unmitigated loss of any remaining archaeological bone. Furthermore, laboratory-based and field experiments have shown that a fluctuating water table in the layer bearing archaeological samples is more detrimental than a stagnant environment (4, 18).

Star Carr has served as an excellent case study, with the rapidity of the geochemical changes allowing the site to be studied on a research-project time scale. However, the implications of this research are global. Although sites with pH as low as that at Star Carr may appear rare, the high oxygen/high sulfur content conditions that have allowed these changes to occur are certainly not unique. Wetlands with high sulfur content occur world-wide, e.g., in the Iberian Peninsula, where extensive pyrite deposits underlie flooded wetlands (40). Coastal wetland areas also typically have high sulfur content originating from the marine environment (41). Because potential threats to wetlands (from pollution, changes in land use, or land drainage) continue to occur on an unprecedented scale (6, 42), it is increasingly likely that other waterlogged archaeological sites are at risk from processes similar to those seen at Star Carr. Although some studies have shown that rewetting of drained archaeological sites can be achieved (5, 43), the success of such a strategy when acidification has already occurred has not, to our knowledge, been investigated. Indeed, the severity of the decay seen in artifacts recently excavated from Star Carr show that any damage caused to the organic remains themselves is rapid and irreversible.

By using a range of macro and molecular analyses, our research has shown that determining the geochemistry of the burial environment is critical in determining the feasibility of preserving organic remains in situ, a policy now pursued globally for archaeological sites. The rapid degradation that we have observed demonstrates that changes in water-management practices in wetland and peatland areas have a significant influence on the preservation of organic remains, with a devastating effect on the value of the archaeological and paleo-environmental information that can be retrieved from these sites. Potential geochemical changes therefore should be considered carefully and should play a role in informing the future management and successful preservation of archaeological sites.

From a chemistry perspective, the tragic deterioration of the Star Carr site has provided a unique opportunity to understand diagenetic processes that normally are invisible over research project time scales. From a cultural heritage perspective, this deterioration is an irreplaceable loss of unique archaeological and environmental evidence, and the lessons learned should be used to safeguard other wetland sites at risk from environmental changes across the globe.

Materials and Methods

Laboratory-Based Burials. Fluctuating and saturated zones for each soil type were set up in identical 25-L fermentation vessels; practical difficulties in achieving low water content at the top of the microcosms meant that separate smaller containers were ultimately used for dry zones. The fluctuating and saturated zones were established by adding deionized water at regular intervals, raising the water level to the top of the fluctuating zone. A tap affixed to the bottom of each microcosm allowed the slow reduction of water levels to the top of the saturated zone, replicating a waterlogged burial environment. Water levels in the fluctuating/saturated zones were monitored by means of a tube affixed to the side of the vessel. Within each zone, a range of types of bone and wood were buried. The material was chosen to be comparable to previously reported experiments in acid only (18, 19) and to provide a comparison of archaeological materials (Table S1).

Analytical Techniques.

Geochemical analysis. Geochemical analysis was carried out immediately upon excavation of a soil sample by the addition of minimal amounts of deionized water. Redox measurements were carried out using a field probe (Hanna Instruments), and pH measurements also were made using a field probe (Hanna Instruments) for in-field measurements or a glass pH probe (Denver Instrument) calibrated between pH 4 and 7 for measurements in the laboratory.

AAR. Bone samples for AAR were prepared in triplicate according to the protocol reported elsewhere (18, 44).

The total amino acid concentration was determined by summing the concentrations of all amino acids present. The original mass of bone then was used to calculate the relative concentrations of amino acid in the bone sample. The degree of racemization in Asx was calculated by determining the concentration of D-Asx and L-Asx to determine a D/L value, or ratio.

p-XRD. All p-XRD analysis was carried out using a Bruker-AXS D8 diffractometer fitted with a copper anode (1.54 λ) and a rotating position-sensitive detector. Powdered bone samples were packed into an aluminum plate with a shallow circular well and were loaded onto a rotating sample holder. For analysis, the X-ray generator was set to 40 kV and 30 mA, and samples were scanned between 24–36 °2θ using a scan rate of 0.3 s per step and an increment of 0.025° (23).

FTIR. A subsample of air-dried wood was sliced with a scalpel. Analysis was carried out on a Vertex 70 FTIR spectrometer fitted with an ATR unit. A resolution of 4 cm^{-1} was used to scan between 600 and 3,600 cm^{-1} using an averaged 16 scans (38).

Py-GC. Surface samples of the wood samples were cut, dried, and ground to a powder. Approximately 1 mg of the powder was weighed in a quartz crucible and placed into a heated filament pyroprobe unit (CDS Pyroprobe 5150; Chemical Data Systems). Samples were cleaned by heating to 290 °C for 15 s in the presence of helium, followed by pyrolysis at 610 °C for 15 s. The pyrolysis unit was coupled to a trace GC Ultra gas chromatograph (Thermo Fisher) fitted with a flame ionization detector and a fused silica capillary column (30 m × 0.25 mm) (Thermo Trace TR-5). The valve oven, transfer line, and GC inlet were held at 310 °C, and the oven temperature was maintained at 50 °C for 5 min; separation was achieved using a ramp rate of 4 °C/min to 320 °C, with a helium carrier gas at 2 mL/min (45). Retention times of key structural compounds were assigned based on published mass spectrometry data (45).

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