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The feasibility of vitrifying a sandstone enclosure in the British Iron Age

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ABSTRACT

Iron Age structures with evidence for having been subjected to high temperatures have been identified throughout Europe. The thermal conditions that must have yielded such evidence of alteration remain enigmatic, especially for the case of high-silica, quartz-rich building materials such as sandstones. Here, we conduct an experimental investigation of thermal treatment using the Wincobank Iron Age hill fort site in Sheffield, South Yorkshire (U.K.) as a test case. We have selected samples of the unaltered protolithic sandstone from which the fort was constructed as starting material as well as material from the vitrified wall core. An experimental suite of thermally treated protolith samples has been analysed using a combined approach involving X-ray diffraction and thermal analysis (simultaneous differential scanning calorimetry with thermogravimetric analysis). Comparison between our experimental products and the variably vitrified samples found in the wall of the Wincobank hill fort helps to constrain firing temperatures and timescales. For mineralogical markers, we employ the high-temperature conversion of quartz to cristobalite and the melting of feldspar to compare the relative abundance of these phases before and after thermal treatment. We find that the Iron Age wall samples have mineralogical abundances most consistent with a minimum firing temperature range <1100–1250 °C and a firing timescale of >10 h. These first quantitative constraints for a fort constructed of sandstone are consistent with those found for forts constructed of granitic material. Finally, we explore the reasons for thermal disequilibrium during firing and invoke this mechanism to explain the differential vitrification found at some Iron Age stone-built enclosures.

1. Introduction

Vitrified forts are anthropogenic archaeological stone-built structures which contain a glass, or devitrified product of a glass, as a phase in the stonework which is surmised to have been produced through in situ exposure to high temperatures. Such forts have been identified throughout Europe (e.g. Youngblood et al., 1978; Kresten, 2004) and are abundant in Scotland (MacKie, 1969; MacKie, 1976; Nisbet, 1974; Friend et al., 2008). Despite a large sample of sites, ambiguity remains concerning the vitrification mechanism, temperatures, kinetics and motives (e.g. Mackie, 1976).

Opinion appears to have converged on a consensus that vitrification is largely an intentional rather than accidental consequence of high temperature treatment of the stonework enclosing the forts (e.g. Youngblood et al., 1978; Nisbet, 1974; Brothwell et al., 1974). The specific prehistoric intentions for vitrification however are not constrained. Hearne (2015) summarises the arguments for intentional vitrification motives in 3 categories: (1) strengthening of the walls (Nisbet, 1974; Brothwell et al., 1974); (2) intentional destructive attack (Cotton, 1954; Small and Cottam, 1972); or (3) a hitherto poorly understood ritual or cultural practice (Bowden and McOmish, 1987). Experimental work constraining the conditions required for vitrification may provide useful insights for deciding the relative likelihood of these three potential mechanisms (e.g. Youngblood et al., 1978). The enigmatic nature of these Iron Age vitrified structures makes them a topic ripe for ongoing study.

The temperatures required for vitrification have been constrained for granitic (sensu lato) building materials to a range with a lower boundary defined by the solidus (~925 °C for dry granites; Youngblood et al., 1978). As there is no direct evidence that complete melting is ubiquitously achieved in any vitrified fort, the upper boundary is likely to be below the liquidus (i.e. <1250 °C for dry granites; Youngblood et al., 1978). Often defined is an upper temperature at which the authors propose that the melt fraction – preserved as glass containing quench crystals produced upon cooling – was in equilibrium with the crystal assemblage (Youngblood et al., 1978; Friend et al., 2007). If the solidus and liquidus are to represent absolute bounds for the vitrification process and if no material-independent general temperature range applies, then the very quartz-rich systems of sandstone-made forts remain substantially less well-constrained than is the case for "granitic" forts.

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Firing of experimentally constructed walls has yielded large-scale confirmation that vitrification is possible in a reconstructed setting using the timber-frame construction thought to be prevalent in the Iron Age (Childe and Thorneycroft, 1938; Ralston, 1986). Similarly, sample-scale experimental work has provided additional constraints on the temperature and timescales required for vitrification (Hearne, 2015; Friend et al., 2008; Friend et al., 2007) although these latter experiments have never been scaled to the conditions likely exhibited in large experimental firings.

Here we use the sandstone building material used in the construction of the Wincobank hill fort site (Sheffield, South Yorkshire, U.K.; Hearne, 2015) to provide a sample-scale experimental suite covering a large temperature (600–1400 °C) and time (0–20 h) window. We compare the thermal and mineralogical results with those from a suite of variably vitrified wall samples at the same fort in order to constrain the range of conditions required to produce the Iron Age examples. Finally, we illustrate an example of the importance of scale when considering the distribution of heat, and therefore vitrification potential, in a sandstone wall. In all of this we build on the work by Hearne (2015) who was the first to employ this experimental approach with Wincobank hill site material.

2. Materials and methods

2.1. Sample selection

Samples were exclusively collected from Wincobank hill fort site (dated to BCE 530–470; Beswick, 1987; Beswick, 1985), which is built from the locally-sourced sandstone (hereafter referred to as the protolith). Samples were selected to represent (1) material that had undergone no thermal alteration and thus can be considered to be the raw protolith material from which the Wincobank enclosure(s) were formed and (2) material from the thermally altered parts of the walls (hereafter referred to as the vitrified samples). The protolith material is ubiquitous in the earthwork construction and outcrops locally as blocks of massive orange sandstone which exhibits minor laminations or small-scale bedding as their only distinguishing textural feature. The vitrified samples found in the site wall differ from the protolith to a variable extent via textural features including red discolouration, black discolouration with a glassy lustre, local vesiculation and fluidal textures (Fig. 1; Hearne, 2015). The specific sampling locations were from various locations on the south side of the enclosure but the poor surface exposure precluded systematic sampling from external to internal edge of the wall itself and we did not undertake excavation. The vitrified samples *Wall 1–4* are chosen to represent the qualitative range of vitrification seen at the site on the grounds of colour and texture.

Fig. 1. A photograph of a vitrified sample from the wall at the Wincobank site, Yorkshire, U.K. (reproduced with permission from Hearne, 2015). The scale bar at the base of the sample is divided into centimetres.

2.2. X-ray powder diffraction (XRD)

In order to discern whether the difference in phases resulting from thermal treatment mimicked that observed between protolith and vitrified samples, the mineralogy of the protolith, the vitrified material and the experimental samples was determined by powder X-ray diffraction (XRD) at the Natural History Museum in London. Samples were ground in an agate mortar and ~50 mg loaded into 6.9 mm diameter, 1 mm depth circular well mounts. XRD data were collected using an Enraf-Nonius PDS120 diffractometer with an INEL 120° curved position sensitive detector (PSD). We used a combination of primary monochromator (Ge 111) and slit system to select only Cu $K\alpha_1$ radiation and define the incident beam size. Tube operating conditions were 40 kV and 35 mA. The angle between the incident beam and the sample surface was maintained at 4.0° with the sample spinning to improve particle statistics. For the detailed investigation of phyllosilicates, an aliquot of each sample was prepared as an oriented mount on a glass slide. This technique encourages preferred orientation of clay particles parallel to the glass slide surface and enhances the intensity of basal reflections (001). A suspension of soil was prepared, sonicated for 1 min and 0.5 ml pipetted onto a clean glass slide and left to dry in air. For this part of the analysis we used a PANalytical X'Pert-PRO diffractometer (240 mm radius) with a step size of 0.02° 2θ, a total count time of 90 min over a scan range of 2–80° 2θ. The PDF-2 database from ICDD (International Centre for Diffraction Data, http://www.icdd.com) was used to perform the phase identification in the diffraction patterns.

The relative proportions of quartz and cristobalite were evaluated using the areal intensities of their highest intensity peaks. A linear baseline was subtracted from the peak associated with quartz at 26.6° 2θ and the peak associated with cristobalite at 21.8° 2θ. The overlap of a minor feldspar peak with the primary cristobalite peak at ~22.0° 2θ (e.g. Damby et al., 2014) was ignored for relative phase quantification since feldspar tended to melt prior to cristobalite crystallisation in our experimental samples (e.g. see Fig. 5) and no wall sample contained both phases.

2.3. Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements were made using a Netzsch® 404 C Pegasus and a Netzsch® 449 C Jupiter, respectively. Samples of protolith and vitrified samples from the Wincobank site were powdered to a particle size distribution with a dominant fraction at 90–125 μm but not further sieved to avoid segregation of phases. 30–40 mg of each was loaded into platinum crucibles with lids. A static air atmosphere was used in all experiments as tests have revealed that the effect of using a more reducing argon atmosphere on the results was negligible within analytical error.

Protolith samples were exposed to two DSC heating cycles. The first cycle was designed to expose the sample to a particular temperature (600–1400 °C peak temperature) for a pre-determined duration (0, 10 or 20 h); the second cycle was to assess the thermal properties imparted to the sample during the first cycle. During both the first and second heating cycles, samples were initially allowed to thermally equilibrate at 100 °C for 20 min. During the first cycle, all samples were heated to the experimental temperature at 25 °C·min^{-1} and held for a dwell time of 0–20 h before cooling at 25 °C·min^{-1} to ambient temperature. During the second heating cycle samples were heated to 1400 °C at 25 °C·min^{-1}. A sampling rate of 40 Hz was used to ensure high resolution. The S-type thermocouples in both the DSC and TG instruments were calibrated to ±1.5 °C. Baseline measurements were made on the same empty crucibles under the same experimental conditions and were subtracted from the sample curves.

Endothermic heat flow peaks interpreted to represent the α–β quartz transition (575–577 °C) were integrated between 550 and 600 °C using a linear regression as a baseline. The integrated value from the second heating cycle is calculated relative to that from the