CAP STRUCTURES AS DIAGNOSTIC INDICATORS OF SILCRETE ORIGIN

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ABSTRACT

Cap structures within silcretes have long been used as a diagnostic indicator of pedogenic silicification. However, a growing number of studies of the micromorphology of non-pedogenic silcretes indicate that this may no longer be appropriate. This paper presents the first systematic investigation of the micro-fabric, geochemistry and mineralogy of cap structures in groundwater silcretes, through an analysis of conglomeratic varieties (puddingstones) from the southern UK. Our results suggest that cap structures in groundwater silcretes fall within a spectrum of types, related to the degree of sorting in the inter-gravel host sediment. At one end of this spectrum are well-defined caps within otherwise well-sorted, overgrowth-dominated silcretes. These caps exhibit a grain-supported fabric, are cemented by micro- and/or cryptocrystalline silica, and contain floating silt-sized quartz and Ti-oxide grains. We propose that these structures developed mainly as a result of in-washing of fine sediments that were subsequently silicified. At the other end of the spectrum are silcretes with caps defined by concentrations of Ti-oxide grains, as opposed to cement type and grain size. These formed mainly as a result of the remobilisation and precipitation of Ti during the silicification of gravels containing interstitial clay-rich sandy sediment. Between these end-members are silcretes with cap structures formed by a combination of in-washing and redistribution of fines plus some local remobilisation of Ti. Overall, the cap structures in this study exhibit a simple micromorphology, lacking the alternating Ti- and silica-rich lamellae typical of pedogenic silcrete. We conclude that the presence of cap structures alone should not be considered diagnostic of pedogenic silicification unless accompanied by other indicators such as a differentiated profile and abundant, complex, way-up structures within the micro-fabric.

Keywords: Groundwater silcrete, micromorphology, silicification, titanium mobilisation

1. Introduction

Silcrete is an indurated geochemical sediment produced by the near-surface accumulation of secondary silica within a soil, sediment, rock or weathered material (Summerfield, 1983; Milnes and Thiry, 1992). It has been described on every continent except Antarctica (Summerfield, 1983), and is recognised as a major terrestrial silicon sink (Basile-Doelsch et al., 2005). To date, four models have been put forward to explain silcrete formation (Nash and Ulliyott, 2007). *Pedogenic silcretes* are those which form as a result of cycles of downward percolation and precipitation of silica within soil profiles (e.g. Thiry, 1978). Non-pedogenic *groundwater silcretes* form under phreatic conditions through silicification at or close to present or former water tables, or at zones of groundwater outflow (Callen, 1983; Thiry et al., 1988; Thiry and Milnes, 1991). Models to explain the origins of non-pedogenic *drainage-line silcretes* and *pan/lacustrine silcretes* are constrained in terms of geomorphological context, with silicification occurring in alluvial fills in contemporary or former fluvial systems or ephemeral lake basins respectively (Young, 1978; Summerfield, 1982; Nash and Shaw, 1998; Shaw and Nash, 1998).

Distinguishing between the various categories of silcrete is of fundamental importance when, for example, attempting palaeoenvironmental reconstruction, establishing sequence stratigraphy or developing engineering ground models, since pedogenic and non-pedogenic silcrete formation takes place over different temporal and spatial scales and in different environmental contexts (Nash and Ulliyott, 2007). A number of diagnostic properties have been proposed to aid recognition. At the macroscale, pedogenic silcretes often exhibit a distinctive profile structure, with columnar and nodular features and a systematic vertical distribution of silica cements (Thiry, 1978; Watts, 1978; Milnes and Twidale, 1983; Thiry and Millot, 1987). In contrast, non-pedogenic silcretes are more massive and lack vertical profile organisation (Summerfield, 1982; Thiry et al., 1988; Nash et al., 1994). Unfortunately, these characteristics are not always clearly developed and are even less likely to be evident in loose boulders or core samples. In these cases, silcrete types may only be distinguished at the microscale.

When viewed in thin-section, non-pedogenic silcretes normally exhibit a simple micromorphology that preserves host sediment structures (Thiry et al., 1988; Milnes and Thiry, 1992; Shaw and Nash, 1998). Pedogenic silcretes, in contrast, have a more complex micromorphology and incorporate a suite of way-up orientated features. These include: (i) tubule-like structures comprising alternating lamellae of silica and anatase; (ii) colloform structures consisting of layered silica and anatase or iron/manganese oxides;

and (iii) pendulous drip-like, stalactitic or beard-like structures developed underneath clasts or on the upper surface of fractures or voids (Frankel and Kent, 1938; Thiry, 1978; Summerfield, 1983; Meyer and Pena dos Reis, 1985; Thiry, 1988; Milnes and Thiry, 1992; Terry and Evans, 1994; Curlík and Forgác, 1996; Ballesteros et al., 1997).

A fourth set of features – silica-cemented conical or cap structures developed on the top of host sediment clasts – is usually added to this list of micromorphological indicators of pedogenesis. Such structures range in size from the millimetre to the sub-metre scale, and typically comprise alternating lamellae of coarser size graded quartz with titaniferous microquartz, sometimes showing cross bedding, graded bedding or reverse graded bedding (Thiry, 1988; Thiry and Simon-Coinçon, 1996; Thiry, 1999; Thiry et al., 2006). These features are often referred to as geopetal caps, cappings or cap-like structures in the silcrete literature (Taylor and Ruxton, 1987; Ulliyott and Nash, 2006; Dupuis et al., 2014). The origin of these structures is not entirely clear, but has been suggested to relate to intermittent but repetitive infiltration events (Thiry and Milnes, 1991), which may reflect an alternation of wet and dry conditions. Many reviews of silcrete formation (e.g. Milnes and Thiry, 1992; Thiry, 1999) treat these cap structures as an exclusive product of pedogenesis. However, caps have also been identified in groundwater silcretes from eastern Australia (Taylor and Ruxton, 1987), and have been observed by one of the authors (DJN) on pebble-sized clasts within groundwater silcretes to the north of Adelaide. Caps have further been documented on the upper surface of coarse sand- to cobble-size clasts in groundwater silcretes from the southern UK (Ulliyott et al., 2004; Ulliyott and Nash, 2006).

Cap structures in groundwater silcretes appear to be less well developed and less pervasive than those found in pedogenic silcretes. However, to date, they have not been described systematically, making it impossible to determine whether they are distinct from their pedogenic counterparts and hence can be used as indicators of silcrete origin. This paper aims to fill this knowledge-gap and, for the first time, document the micromorphology and geochemistry of cap structures within groundwater silcretes. It does so through the analysis of groundwater silcretes from various sites across the southern UK (Fig. 1; Table 1). We focus upon groundwater silcretes developed within gravel-rich, as opposed to predominantly arenaceous, host sediments, since caps are larger and better developed in these materials. On the basis of a range of analyses we discuss the possible origin of cap structures within groundwater silcretes and propose guidelines for the wider use of such way-up orientated features in distinguishing different silcrete types.

2. Background and study areas

2.1 Silcretes in the southern UK

Silcretes are widespread across the southern UK and occur typically as dislocated boulders on the late Cretaceous Chalk, in close association with a number of Palaeogene arenaceous formations, or with the Clay-with-Flints Formation or Pleistocene sediments (Summerfield and Goudie, 1980). Three types of silcrete are recognised on the basis of host sediment type and variations in induration. Those that formed in sandy host materials (termed *sarsens* in the UK literature) can be divided into a *saccharoid* or quartz arenite type, and an *extremely hard* type which varies from quartz arenite to quartz wacke (Prestwich, 1854; White, 1925; Summerfield and Goudie, 1980). The saccharoid type most commonly exhibits a grain-supported (GS-) fabric (*sensu* Summerfield, 1983) with optically-continuous quartz overgrowths and subsidiary microquartz and/or cryptocrystalline silica cements (hereafter referred to as a saccharoid fabric). In the extremely hard variety, cryptocrystalline silica or microquartz cements are dominant, either within a GS- or floating (F-) fabric (Summerfield and Goudie, 1980; Summerfield and Whalley, 1980; Howard, 1982; Ulliyott et al., 2004; Ulliyott and Nash, 2006).

Gravel-rich variants of the above – the focus of this study – define the third silcrete type, and include silica-cemented conglomerates, breccio-conglomerates and breccias. Such silcretes are commonly termed *puddingstone*. Greater micromorphological variability is typical in gravel-rich silcretes; many have an arenaceous GS-fabric matrix in between gravel clasts, although both F- and matrix (M-) fabrics (suggestive of a clay-rich inter-gravel matrix prior to silicification; cf. Smale, 1973; Dewers and Ortoleva, 1991) have been described (Kerr, 1955; Skipper, 1999).

A non-pedogenic groundwater origin has been proposed for most silcretes in the southern UK on the basis of the absence of complex profile structures and the tabular macromorphology and simple micromorphology of most boulders (Ulliyott et al., 1998; Ulliyott et al., 2004). Silcrete formation has traditionally been attributed to the Palaeogene (e.g. Jones, 1999), though silicification in the Late Neogene during the course of landscape dissection and erosion of Palaeogene sediments has been suggested (Ulliyott et al., 1998; Ulliyott et al., 2004; Ulliyott and Nash, 2006).

2.2 Sampling localities

Gravel-rich groundwater silcretes occur in four main areas of southern England (Table 1). In all varieties, flint, derived from the late Cretaceous Chalk, is the predominant gravel

clast type. The Hertfordshire and Bradenham puddingstones (northern and northwest London Basin respectively) are the best documented, and can be distinguished by the presence of more angular pebbles embedded within the Bradenham variant (Davies and Baines, 1953). The Hertfordshire Puddingstone occurs on the Chalk and both on and within Lambeth Group (Palaeocene) sediments (which overly the Chalk unconformably). The only well documented *in situ* occurrences of puddingstone occur in Hertfordshire, within the Upnor Formation, the basal unit of the Lambeth Group (Moffat and Catt, 1983; Robinson, 1994; Lovell and Tubb, 2006). The Upnor Formation is predominantly arenaceous, is characterised by a basal flint gravel and sometimes by gravelly intercalations, and is considered the most likely host sediment in which silcrete formation occurred (Small, 1980; Young and Lake, 1988). Bradenham Puddingstone occurs principally fringing the Palaeogene outcrop in association with Clay-with-Flints *sensu lato* (Loveday, 1962), which largely comprises Lambeth Group sediments reworked during the Plio-Quaternary (Catt, 1986). Breccio-conglomeratic silcretes also occur in the western Weald of Hampshire, where they are found overlying the Chalk in, or downslope from, outcrops of the Clay-with-Flints Formation (White, 1910; Bury, 1922). There are no clear relationships to existing Palaeogene sediments in this area, although in the southern Weald of Sussex, gravel-rich breccia silcretes occur in Plio-Quaternary Clay-with-Flints and in, or adjacent to, disturbed arenaceous facies of the Lambeth Group (Ullyott et al., 2004). In all of these localities, conglomeratic silcretes occur as displaced blocks or boulders, with a universally simple macromorphology comprising large tabular blocks. Puddingstone is also found in Pleistocene (e.g. Chalk Head – in part of periglacial origin) and Holocene sediments as smaller sub-rounded boulders (e.g. at Seaford and Chyngton, East Sussex).

3. Materials and methods

Samples were collected from eight localities within the four areas of gravel-rich groundwater silcrete occurrence (Fig. 1). The macromorphological characteristics and field relations of the silcretes at each site are described in Table 1, with the suite of techniques applied to each sample shown in Table 2. Samples were initially examined in hand specimen to establish the nature and extent of cap structures, and then in thin-section to determine variations in micromorphology between the caps and other areas of the silcrete matrix. Polished thin sections were also studied by scanning electron microscope (SEM) to determine the nature of silcrete microstructures. Colour-cathodoluminescence (colour-CL) images were obtained from a subset of the polished thin sections, using a Zeiss EVO SEM

with a Gatan Chrome CL attachment. In order to allow images to be obtained without beam damage occurring to the quartz, a beam dosage of 3nA at 20kV and a short dwell time of 20 microseconds were used. Backscattered scanning electron microscope (BSEM) analyses were utilised both for petrographic study and to investigate mineralogy, with SEM X-ray analysis (XRA) used to provide a qualitative identification of mineral components. SEM energy dispersive X-ray spectroscopy (EDS) line analyses and elemental maps were conducted on polished thin sections, both across caps and, as a control, across clast/matrix interfaces where caps were not developed. Micro-X-ray diffraction (μ XRD) analyses were performed on three bulk samples to identify the Ti-oxides present. To obtain a concentrate of the Ti-oxides, quartz grains and cements were dissolved using 48% hydrofluoric acid heated to 80°C, with the residue washed with distilled water and dried prior to analysis. μ XRD analyses were carried out using a Siemens PSD X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation, with samples scanned on silicon wafers with a 0.02° step width, and 0.2 mm slits, from 5 to 70° 2 θ .

4. General silcrete fabrics away from cap structures

Prior to providing details of the micromorphology and geochemistry of cap structures within gravel-rich groundwater silcretes, it is necessary, for comparative purposes, to describe silcrete fabrics in inter-gravel areas of samples *away from* silica-cemented caps. Induration in these areas varied from very well cemented with a splintery conchoidal fracture (*extremely hard* type) to less well and patchily cemented with a porous appearance (*saccharoid* type). The majority of samples exhibited a GS-fabric with a simple micromorphology, as described previously for UK groundwater silcretes (Summerfield, 1979; Summerfield and Whalley, 1980; Howard, 1982); nodular, glaeular or illuvial colloform structures were not observed. There were, however, variations in general fabric both within and between sites. These can be attributed to differences in the silcrete host material, specifically (i) the dominant grain size and degree of sorting of inter-gravel arenaceous sediments, and (ii) the proportion of gravel present.

Silcretes with moderately well- to poorly-sorted sandy inter-gravel sediment (e.g. Bradenham – Fig. 2a; Bramdean; Goldstone Valley – Fig. 3a; Ley Hill, sample LY6) were moderately to well indurated, usually with a fracture around the detrital grains (typical of saccharoid fabric). Inter-gravel sediments in these samples typically exhibited a GS-fabric cemented by optically-continuous quartz overgrowths (Fig. 2b, Fig. 3b). Many areas of overgrowths displayed polygonal contacts typical of groundwater silcretes elsewhere

208 (Thiry et al., 1988; Thiry, 1999). Minor amounts of cryptocrystalline silica were present
209 along grain contacts, in primary void spaces and in patches between larger pebble-sized
210 clasts. Some residual porosity was invariably present and there was evidence of late
211 infiltration of clay and minor dissolution of quartz grains and silica cements post-dating
212 silcrete formation (cf. Ulliyott and Nash 2006). Dissolution was more common in
213 ferruginised samples, with opaque minerals forming partial or complete void fills. More
214 rarely (e.g. Goldstone Valley, sample GS1), ferruginisation was pervasive with almost total
215 dissolution of the overgrowth fabric, a considerable increase in porosity, and re-
216 cementation by iron oxides. It was clear that such ferruginisation postdated silcrete
217 formation as the ferruginous cements were superposed on, or crosscut, pre-existing silica
218 cements (cf. Ulliyott et al. 2004).

219 More poorly-sorted silcretes that contained significant inter-gravel silt and clay (e.g.
220 Brightstone Lane – Fig. 4a; Chyngton; Seaford Head – Fig. 5a) also typically exhibited GS-
221 fabrics, but the distinction between cap and non-cap fabric was less clear. Cement types
222 were variable, concomitant with differences in the degree of induration observed
223 (transitional between saccharoid and extremely hard types) and in relation to the
224 distribution of finer detrital material. In very poorly sorted silcretes with high proportions of
225 gravel (e.g. Brightstone Lane; Seaford Head), the non-cap fabric comprised a minority of
226 the silcrete due to the large size and abundance of caps present. Optically-continuous
227 quartz overgrowths occurred in areas with fewer fines, and were most often seen beneath
228 and/or in thin gaps between gravel clasts (Fig. 4b, Fig. 5b). Overgrowths displayed
229 gradational contacts with microquartz or cryptocrystalline silica cements, which
230 characterised areas with greater silt and clay content. In very poorly sorted silcretes with a
231 lower proportion of gravel (e.g. Chyngton), cement types were very variable reflecting the
232 patchy distribution of the finer detrital component. In these samples, optically-continuous
233 overgrowths were dominant in areas with less finer-grained detrital material; mixed fabrics
234 with quartz overgrowths and either microquartz and/or cryptocrystalline silica occurred in
235 areas with more silt and clay (cf. Ulliyott and Nash, 2006).

236 Silcretes completely lacking in quartz overgrowth cements were encountered only in the
237 Hertfordshire Puddingstone at Ley Hill (LY2, Fig. 6a) and Bovingdon. These were the most
238 consistently well-indurated silcretes and exhibited a splintery or subconchoidal fracture
239 (extremely hard fabric type). Once more, GS-fabrics were dominant and comprised fine
240 sand-sized detrital grains in a cryptocrystalline silica or microquartz cement that was
241 characterised by some detrital silt and ubiquitous opaque grains (Fig 6b,c). Some detrital

grains exhibited diffuse or fretted boundaries and gradations to F-fabric were observed. More rarely, the distribution of opaque grains in areas of framework-poor matrix was suggestive of poorly developed curved or 'cusplate' segregations or patches (Fig. 7). A single sample from Ley Hill (LY5) exhibited an M-fabric inter-gravel matrix, presumably representing an originally clay-rich host material now replaced by cryptocrystalline silica (cf. Smale, 1973) with minor sand- and silt-sized detrital quartz grains.

5. Fabrics within cap structures

Clearly defined cap structures, or more diffuse areas of cementation on the upper surface of pebble- or cobble-sized clasts, were present in silcretes from every site investigated. Only in the Hertfordshire puddingstone were there rare examples in which few or no caps were observed. Typical cap features varied in size from millimetres (Fig. 6a) to centimetres (Fig. 2a) thick. The scale of cap development generally increased with the size of the host sediment clast, although there was considerable variation between samples and between geographical localities. In many clast-rich silcrete conglomerates and breccias, cap structures were so extensive and coalescent that they comprised the majority of the silcrete fabric (e.g. Goldstone Valley, sample GS2 – Fig. 3a; Seaford Head – Fig. 5a), while at other sites caps were restricted to a few of the larger clasts only (e.g. Bramdean; Ley Hill, sample LY6).

In silcretes with a well- to moderately-sorted arenaceous 'saccharoid' matrix, caps were easily discerned in hand specimen by their darker grey or pale buff colour and denser cementation (e.g. Bradenham, sample BD2 – Fig. 2a; Goldstone Valley, sample GS2 – Fig. 3a). Porosity differences between the cap and non-cap silcrete fabric were often marked by a thin rim of iron staining along the upper edge of the more densely cemented cap. Less commonly in strongly ferruginised saccharoid fabrics (e.g. Goldstone Valley, sample GS1), the caps remained comparatively unaltered while the rest of the silcrete fabric was almost entirely replaced by iron oxides.

Cap features were less clearly defined in the very poorly-sorted clast supported gravel-rich silcrete from Brightstone Lane (Fig. 4a). The degree of cementation was strongly influenced by the distribution of gravel clasts, with well cemented cap features on upper surfaces of clasts (Fig. 4c) and more porous or friable cements beneath or in narrow gaps between clasts. In the most strongly cemented silcrete breccias and conglomerates, cap features varied from well-defined buff-stained caps on pebble and granule sized clasts (e.g. Ley Hill, sample LY2; Fig. 6a), through more diffuse brownish-stained densely-

275 cemented way-up orientated areas of cement (e.g. Seaford Head – Fig. 5a; Chyngton, see
276 Fig. 4b in Ulliyott and Nash, 2006), to silcrete where caps were hard to distinguish in hand
277 specimen (e.g. Bovingdon Green) or absent altogether (Ley Hill, sample LY5).

278 Despite the variations noted above, cap features were consistent in their
279 micromorphology. In silcrete with well-defined caps and overgrowth-dominant GS-fabrics
280 (e.g. Bradenham, Bramdean, Goldstone Valley), the cap fabric was also of GS-type but
281 cemented by micro- and/or cryptocrystalline silica (Fig. 2c, Fig. 3c). Optical thin section,
282 colour-CL and BSEM analyses indicated that, within the cap, the host sediment was
283 notably more poorly sorted than in the surrounding silcrete fabric, and was richer in quartz-
284 rich fine sand, silt and detrital heavy minerals (Fig. 8a-d; Fig. 9a,b). In one sample (LY6,
285 Ley Hill), muscovite occurred in the cap but was absent from the ordinary matrix. Caps
286 characteristically had lower sand-sized host sediment grain contents than the surrounding
287 silcrete fabric and *some* of the incorporated grains showed diffuse or fretted boundaries
288 (Fig. 3c, Fig. 8a). The cap fabric also contained disseminated opaque grains (in the size
289 range 5-20 µm; Fig. 9b) which typically increased in size and/or number toward the host
290 clast. Concomitant with this, silica crystal size in the cap cement often decreased from
291 microquartz in the upper part of the cap to cryptocrystalline silica towards the contact with
292 the host pebble or cobble. Some build-up of opaque minerals or illuvial clays was
293 characteristic of voids within areas of overgrowth fabric bordering cap structures. In
294 strongly ferruginised silcrete (e.g. Goldstone Valley, sample GS1), the upper parts of caps
295 were impregnated with opaque minerals, with evidence of brecciation, dissolution and
296 replacement of the silcrete fabric. Thin encrustations of microquartz were occasionally
297 present on flint clasts away from, or marginal to, the cap feature itself (cf. Summerfield and
298 Whalley, 1980) and, less frequently, cryptocrystalline silica outgrowths occurred from flint
299 clasts.

300 The less defined caps noted in clast-rich silcretes from Brightstone Lane had more
301 transitional boundaries, with areas of mixed quartz overgrowth and micro- and/or crypto-
302 crystalline silica cements grading into typical cap fabric lacking overgrowths. This variation
303 was closely related to the distribution of the finer grained silt- and clay-sized sediment. In
304 some caps, host sediment grain size diminished toward the pebble or cobble clast (Fig.
305 4c). Contacts between caps and host flints were sometimes diffuse in thin-section, as the
306 grain size of the silica cement within the cap was very similar to that within the flint. Some
307 ferruginisation of the upper surface of the flint and the lower section of the cap matrix was
308 also noted.

The diffuse areas of brown way-up orientated cement clearly discernible in hand specimen in silcretes from Seaford and Chyngton were less easily identifiable in thin-section. They appeared to be characterised by more poorly-sorted areas, with microquartz or cryptocrystalline cements (e.g. Fig. 5c) predominant over optically-continuous quartz overgrowths. Thin cap features were distinguishable on granules and coarse sand grains, evidenced by an increased content of 1-40 μm opaque grains in caps cemented by microquartz or by dark brown/opaque cryptocrystalline silica cement. Caps within the clast-supported silcrete conglomerate from Seaford exhibited a GS- to F- fabric with brown cryptocrystalline silica cement that was often almost opaque (Fig. 5c).

In silcrete conglomerates and breccias with a GS- to F-fabric matrix and microquartz cements, as in some examples of the Hertfordshire puddingstone, there was less contrast between the cap and non-cap silcrete fabric, as both contained quartz silt. Caps were defined by an increased content of opaque grains in the microquartz cement (e.g. Ley Hill, sample LY2 – Fig. 6b,c) or by dark brown/opaque cryptocrystalline silica cement (e.g. Bovingdon Green), and in some cases by reduced numbers of sand-sized detrital grains (Fig. 6b,c).

6. Geochemistry of cap structures

Previous work has identified Ti, Al and Fe as the principal non-silica constituents of UK silcretes (Summerfield, 1979; Summerfield and Whalley, 1980; Ulliyott et al., 2004; Ulliyott and Nash, 2006). The results of this study confirm this finding. μXRD analyses indicated that the dominant Ti mineral is rutile, with minor anatase present in most samples. BSEM imaging indicated that a significant proportion of the rutile grains were weathered and are therefore likely to be of detrital origin. Ti was consistently detected within caps, with EDS line scans (Fig. 10) showing significantly higher concentrations than in the surrounding matrix. Element maps indicate a few larger (up to 40 μm) discrete grains within caps but with numerous cryptocrystalline particles (<1 μm) also present. In some caps, grading is discernible, with numbers of Ti particles increasing toward the clast surface. In three samples (BD2, LY2, LY6), a thin line of Ti enrichment is present at the interface between caps and host clasts, particularly for larger clasts (Fig. 11). Significantly, no linear, cusped or colloform features were identified during Ti element mapping. Ti-oxide grains are less common within areas of quartz overgrowth cement away from caps, but, where present, are at the upper end of the size range. In samples dominated by cryptocrystalline silica and microquartz cements (e.g. sample LY2; Fig. 11), Ti is more evenly distributed between cap and non-cap fabrics with a mixture of size ranges present in both fabrics.

EDS line scans and element maps indicated that the majority of caps additionally contain Al. The Al-containing mineral has not been identified as it is present below μ XRD and EDS detection limits. Patterns of Al distribution are not as clear as for Ti, with Al irregularly distributed throughout caps. In samples with a dominant quartz overgrowth cement, Al is typically found at the interface between cap structures and the surrounding quartz overgrowth fabric (e.g. Fig. 10). In this situation, thin-section evidence is consistent with the Al being contained in clay minerals washed through the pore network of the silcrete, along with Fe oxides, after the main phase of silicification. Fe oxide is not significantly present within cap structures. Instead, BSEM and optical petrography analyses shows that Fe oxides line and infill pores at the interface between caps and adjacent areas of quartz overgrowth cement. In more ferruginised silcretes (e.g. samples GS1, GS2), Fe oxides partially replace both quartz grains and silica cements in the upper parts of caps.

7. Discussion

7.1 *Origins of cap structures*

The cap features within groundwater silcrete described in section 5 are distinct from those documented in pedogenic silcrete, in that: (i) they have a simple structure lacking systematic organisation; (ii) the alternating lamellae of Ti-poor quartz and Ti-rich microquartz, characteristic of pedogenic silcretes in France and Australia (Thiry, 1988; Thiry and Simon-Coinçon, 1996; Thiry, 1999; Thiry et al., 2006), are completely absent; and (iii) features such as reverse-graded bedding and cross bedding within caps, also reported from pedogenic silcretes in these countries, are not present (although some normal-grading of Ti-oxide grains was evident). The simplicity of the cap structures identified in this study is mirrored by the equally simple micromorphology of the general silcrete fabric.

Cap structures within pedogenic silcretes are a direct product of the silicification process, whereby silica and other components percolate downwards through the profile in intermittent but repetitive cycles of flushing and precipitation (Milnes and Thiry, 1992). This produces the characteristic lamellar structures present within caps, as well as the many other way-up orientated features found in pedogenic silcrete fabrics (see section 1). In contrast, the micromorphology of the cap structures within the groundwater silcretes described here indicates that caps of fine sediment were present above gravel clasts *prior*

375 to silicification; much of this sediment was replaced during the silicification process to
376 leave a silica-cemented cap.

377 There are three main lines of evidence to support the existence of sediment caps prior
378 to cementation. First, the cap structures in this study consist of (mostly) quartz framework
379 grains with interstitial floating quartz-rich silt, cemented by microquartz and/or
380 cryptocrystalline silica. The floating grains must have been supported by a pre-existing
381 material otherwise they would have collapsed to the bottom of pore spaces; the
382 dominance of microquartz and/or cryptocrystalline silica cements, as opposed to optically-
383 continuous quartz overgrowths, within the cap fabric strongly suggests that this material
384 was clay-rich (Smale, 1973; Dewers and Ortoleva, 1991). Second, the cement and floating
385 silt within caps infill primary pore spaces between framework grains, indicating that this
386 finer material must have been present prior to silicification. Third, at the margins of caps,
387 the microquartz and/or cryptocrystalline silica cements exhibit both interlocking and
388 gradational contacts with the surrounding overgrowth fabric (cf. Ulliyott and Nash 2006),
389 suggesting simultaneous and competitive growth. This could not have occurred in the
390 absence of a fine sediment infill between framework grains. The distribution of Ti within
391 cap structures (section 6) may provide further clues as to the relative timing of cap
392 sediment accumulation. μ XRD analyses of bulk samples identify rutile as the main Ti-
393 bearing phase, with BSEM imaging indicating that much of this is detrital in origin. EDS
394 line analyses and elemental maps further indicate that Ti is concentrated within caps. By
395 inference, it would appear likely that a proportion of Ti-oxide grains within caps
396 accumulated as part of the detrital fine sediment component prior to silicification. Anatase
397 may, however, also be present within caps (see below), which suggests an additional
398 phase of authigenic Ti-oxide formation during the course of silicification.

399 Whilst the existence of fine sediment caps prior to silicification is clear, the precise origin
400 of these sediments is less certain. Ulliyott et al. (2004) have suggested three options: (i)
401 the caps are primary sedimentary structures inherited from the host sediment; (ii) they
402 were formed by in-washing of fines through a sandy host material as a synsedimentary
403 process (e.g. as suggested by Frostick et al., 1984, to explain the presence of fine
404 matrices within coarse-grained alluvial sediments); or (iii) infiltration of fines may have
405 occurred as a result of diagenesis, but prior to silicification, while groundwater was
406 circulating through the sediment. Ulliyott and Nash (2006) argued for (ii) from the analysis
407 of a limited number of cap structures but noted that the precise mechanism by which clay
408 and silt infiltration occurred is unclear. Many of the observations in section 5 could be

explained by the in-washing of fine sediments from *outside* the host formation (i.e. options ii and iii), possibly from adjacent clay-rich beds, and their accumulation above gravel clasts (cf. Ulliyott and Nash (2006). However, some observations are more compatible with the redistribution of fines from *within* an originally silt-clay bearing host material by circulating groundwater (effectively a refinement of option iii). Such a mechanism was recently evoked to explain 'geopetal cappings' on sporadic flint clasts found within groundwater silcretes developed in early Palaeogene sands in Normandy, France (Dupuis et al., 2014). The relative importance of in-washing vs. redistribution may be a function of sorting of the host sediment. More clearly defined caps are characteristic of better sorted host materials. This is logical, since better sorting would have led to higher porosity and facilitated the infiltration and accumulation of fine cap sediment. In contrast, less well defined caps, with more gradational contacts between the cap and surrounding non-cap silcrete fabric, characterise more poorly sorted host materials; in these instances, in-washing of cap sediment would have been hindered by the lower permeability and porosity. In such poorly sorted host sediments, redistribution may be the main mechanism to explain the development of cap structures.

This study has also revealed some groundwater silcretes which contain cap structures that exhibit no evidence for either infiltration or redistribution of sediment in their formation. In these rare instances, the sedimentary component of the cap must be a primary structure inherited from the host sediment (i.e. option i above). An example of this can be seen in Fig. 6b,c (sample LY2), where an F-fabric occurs at the base of the cap. This feature can only be explained by the presence of primary fine sediment, now replaced by silica, since without this fine sediment, the overlying framework grains would have collapsed into a void. This sample has a predominantly GS-fabric and a microquartz and cryptocrystalline silica cement, compatible with a host sediment comprising framework grains and clay-rich interstitial material. The cap as a whole is characterised by a much larger area of dark colouration due, in part, to enhanced concentrations of very small Ti-oxide grains. The increase in smaller Ti-oxide particles observed within the cap fabric towards the host clast, the accumulation of Ti-oxides at the base of the cap, and the presence of poorly developed cusped features (Fig. 7), suggests there was some local remobilisation (e.g. via release from clay mineral lattices) and precipitation of authigenic Ti-oxide during silicification. Such mechanisms have been advocated to explain Ti-rich features within silcretes developed in clay-rich sediments elsewhere (Webb and Golding, 1998), and may also help explain Ti distribution patterns in better sorted silcretes within this study (e.g. samples BD2 and LY6 – see section 6). However, further analysis is required to determine

the relative proportions of detrital or authigenic Ti-oxides within caps. It may be that the bimodal size distribution of Ti-oxide grains identified by element mapping reflects larger (c. 40µm), and hence volumetrically dominant, rutile and smaller (<1 µm) cryptocrystalline anatase.

Overall, the results of this study suggest that cap structures within groundwater silcretes fall within a spectrum of types. At one end of this spectrum are well-defined caps occurring within otherwise 'clean', well-sorted, overgrowth-dominated silcretes (e.g. samples BD2, GS2). These structures are likely to have developed mainly as a result of in-washing of fine sediments, which were subsequently silicified. At the other end of the spectrum are silcretes with caps mainly defined by dark colouration (due to concentrations of Ti-oxide grains) developed in poorly sorted clay-rich sediments (e.g. samples LY2, BV1). In these cases, there is little evidence for in-washing or redistribution of fine sediment. Instead, cap structures have developed predominantly as a result of the remobilisation and precipitation of Ti during silicification. In between these end-members are silcretes exhibiting cap structures formed by a combination of in-washing and redistribution of fine sediments plus some local remobilisation of Ti.

7.2 Comparison with studies in eastern Australia

As noted in the introduction, the only other place where equivalent cap structures have been documented in groundwater silcretes is the Shoalhaven area of eastern Australia (Taylor and Ruxton, 1987). In this area, caps at the scale of <1 mm in thickness occur on sand-sized host sediment clasts. The Shoalhaven caps show similarities to those described in this study, including grading of Ti-oxide particles, and Ti-oxide coatings on the host clast surface. Characteristically there is also an absence of alternating Ti-rich and Si-rich lamellae within the caps. The small size of these cap features suggests that infiltration or redistribution of fines within the host sediment did not occur on anything like the same scale as the silcretes in this study.

In contrast to the UK caps, the Shoalhaven examples occur as part of a 'complex array of geopetal fabrics' (Taylor and Ruxton, 1987, p. 401). These fabrics comprise cusped convex or concave upward features, or graded accumulations of anatase, which are more common and more clearly developed than any found in this study. However, their position within the silcrete – only in patches exhibiting an F- or M-fabric with limited framework grains – is similar to the examples described here. Taken as a whole, the caps within the Shoalhaven silcretes show greatest similarity to those UK examples developed in poorly

477 sorted clay-rich sediments, suggesting that both caps and other associated way-up
478 orientated features resulted mainly from redistribution of Ti during silicification.

479 **8. Conclusions**

480 This study is the first to document systematically the micromorphology, geochemistry and
481 mineralogy of cap structures within groundwater silcretes, through the examination of way-
482 up orientated features within conglomeratic silcretes from the southern UK. Cap structures
483 fall within a spectrum of types. One end-member is represented by caps developed mainly
484 by in-washing of fines through well-sorted inter-gravel sediments, with this fine material
485 subsequently silicified. Caps in these sediments are well-defined, exhibit a GS-fabric
486 cemented by microquartz and/or cryptocrystalline silica, and contain floating silt-sized
487 quartz clasts and Ti-oxide grains. The other end-member comprises caps that are defined
488 by their darker colour, reflecting a higher content of Ti-oxide grains, developed in poorly
489 sorted, originally clay-rich, sediments. These have a GS- to F-fabric, are also cemented by
490 microquartz and/or cryptocrystalline silica, but formed mainly due to the mobilisation and
491 reprecipitation of Ti during silicification. In between these extremes are cap structures
492 formed by in-washing and/or redistribution of fine sediments prior to cementation, with
493 some evidence for local remobilisation of Ti during silicification. Such caps are often less-
494 well defined and tend to occur in silcretes with more poorly sorted inter-gravel sediments.

495 It is clear from our results that visible cap structures are not unique to pedogenic silcrete
496 and should not, therefore, be used as a diagnostic indicator of silcrete type unless
497 accompanied by detailed micromorphological analyses. In contrast with caps in pedogenic
498 silcretes, the structures described here developed mainly *prior to*, as opposed to being
499 exclusively a *product of*, silicification. Cap features in groundwater silcretes appear to be
500 characterised by a much simpler structure and lack the alternating Ti- and silica-rich
501 lamellae which occur within pedogenic silcrete caps. This echoes the distinction already
502 drawn between the simple fabrics of non-pedogenic silcretes and complex fabrics of
503 pedogenic varieties (Milnes and Thiry, 1992). Some groundwater silcretes in this study
504 show evidence of local redistribution of Ti to form poorly defined segregations both within
505 caps and the wider silcrete fabric, but this is relatively rare.

506 In line with the approach used by Médard Thiry and colleagues, we recommend that
507 both macromorphological and detailed micromorphological analyses are used, wherever
508 possible, to distinguish silcrete types. Critically, it is not the simple presence of individual
509 indicators that provide clues to silcrete origin but their combination, abundance and degree
510 of development. For example, a silcrete exhibiting visible cap features and a clear

511 columnar structure at the macroscale, with abundant, well-developed way-up orientated
512 features at the microscale, will almost certainly have formed as a result of pedogenesis. In
513 contrast, a silcrete with visible caps and no clear differentiated profile could have
514 developed via either pedogenic or groundwater silicification. There is, for example,
515 growing evidence that columnar structures may not be an essential feature of pedogenic
516 silicification (Quesnel et al., 2003). Furthermore, columns may have developed at too large
517 a scale to be discernible in small exposures (Thiry and Simon-Coinçon, 1996). In such
518 cases, systematic analysis is essential to determine the micromorphology of the cap
519 structures, the range and abundance of other way-up orientated features (if any), and
520 hence determine the mechanism of silcrete genesis.

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674

Table 1: Characteristics of gravel-rich groundwater silcretes in the southern UK (MQ indicates microquartz; CCS cryptocrystalline silica).

Geographical area	Locality	Associated sediments	Lithology	Clast types	General silcrete fabric	Cap features	Cap fabric
Hertfordshire Puddingstone, northern London Basin	1. Ley Hill, Chesham, Buckinghamshire 51°41'40.57"N; 0°34'05.61"W	Pebbly clay and sand over the Chalk; fringing outlier of Palaeocene-Eocene sediments	Clast- to matrix-supported conglomerate to pebbly sandstones with sandy or fine-grained matrix	Very well-rounded to rounded flint pebbles, some smaller shard-like flint	GS-fabric quartz overgrowth cements; GS-to F-fabric with MQ to CCS cements; M-fabric with CCS cement	Clearly defined buff-coloured caps on pebbles in some samples, others have few or no caps	GS- to F-fabric; MQ to CCS toward flint; opaque minerals increase in size toward flint, quartz silt and heavy minerals, some fretted quartz grains
	2. Bovingdon Green, Buckinghamshire 51°43'00.88"N, 0°32'34.54"W	In Clay-with-flints over the Chalk	Clast-supported conglomerate with fine, well-sorted sandy matrix	Very well-rounded red-stained flint pebbles, some smaller shard-like flint	GS-fabric with MQ and CCS cement	Colour variations suggest possible cap features	GS fabric; MQ to CCS toward flint; opaque minerals increase in size toward flint.
Bradenham Puddingstone, north-west London Basin	3. The Coppice, Bradenham, Buckinghamshire 51°40'05.42"N, 0°47'45.91"W	On/in Chalk Head over the Chalk, downslope from Clay-with-Flints	Breccio-conglomerate to pebbly moderately- to poorly-sorted sandstone	Subrounded to sub-angular flint pebbles to cobbles	GS-fabric, with quartz overgrowth cements (minor MQ and CCS)	Well-defined thick caps on flints are darker grey and with better cementation	GS-fabric with MQ and CCS; opaque minerals increase in size toward flint, quartz silt and heavy minerals, some fretted quartz grains
Alton, Hampshire, western Weald	4. Brightstone Lane, Farringdon, Hampshire 51°06'28.61"N, 1°00'45.04"W	On/in Chalk Head over the Chalk, down slope from sandy Clay-with-Flints	Clast-rich breccio-conglomerate to conglomerate with very poorly sorted coarse sandy/pebbly matrix	Rounded to irregular flint pebbles to cobbles; sub-rounded pebbles of quartz and quartzose lithics	GS-fabric quartz overgrowth cements (minor MQ and CCS)	Poorly defined, thick well-indurated caps; voids or friable material beneath pebble clasts	GS-fabric; MQ to CCS toward flint, opaque minerals increase in size toward flint, quartz silt & heavy minerals, some fretted quartz grains
	5. Bramdean, Hampshire 51°02'26.35"N, 1°06'12.29"W	On Chalk Head over the Chalk, fringing Clay-with-Flints	Pebbly sandstone to breccio-conglomerate with moderately well-sorted sandy matrix	Sub-rounded to angular flint pebbles	GS-fabric quartz overgrowth cements (minor CCS)	Well-defined caps delineated by rim of iron stain and better induration	GS-fabric MQ cement; opaques, quartz silt and heavy minerals, some fretted quartz grains
South Downs, southern Weald	6. Goldstone Valley, Hove, East Sussex 50°50'46.29"N, 0°08'09.65"W	On the Chalk downslope from disturbed Palaeocene outlier	Breccia with poor- to moderately-sorted quartzose sandstone matrix	Angular to irregular flint pebbles to cobbles, some smaller shard-like flint	GS-fabric quartz overgrowth cements (some ferruginisation)	Well defined thick caps on flints are darker grey with better induration	GS-fabric, MQ and CCS; opaque minerals increase in size toward flint; quartz silt, some fretted quartz grains
	7. Chyngton, Seaford, East Sussex 50°45'55.57"N, 0°08'09.65"E	On outlier of disturbed Palaeocene sediments	Matrix-supported breccia with very poorly sorted sandstone matrix	Angular to irregular flint pebbles to cobbles with some flint shards	GS-fabric quartz overgrowth grading to MQ / CCS cements	Poorly defined brown-stained cap areas above clasts	Dark stained CCS, quartz silt, some fretted quartz grains
	8. Seaford Head, East Sussex 50°45'29.52"N, 0°07'21.31"E	On recent beach near Clay-with-Flints, fringing a Palaeocene outlier	Clast-supported conglomerate with poorly sorted fine to coarse sandstone matrix	Rounded to well-rounded flint pebbles	GS-fabric quartz overgrowth, MQ and CCS cements	Very extensive brown-stained cap areas above clasts; more porous grey fabric under clasts	GS-fabric (to F-fabric in parts), dark stained CCS; opaques grains and staining, fretted/diffuse grain boundaries

Table 2: Range of analytical techniques applied to each sample.

Geographical area	Locality	Sample	Hand specimen	Thin section	CL	BSEM with XRA	Elemental mapping	Line analysis	Micro-XRD
Hertfordshire Puddingstone, northern London Basin	1. Ley Hill, Chesham	LY1	x						
		LY2	x	x	x	x	x	x	
		LY3	x						
		LY4	x						
		LY5	x	x			x		
		LY6	x	x			x	x	
	2. Bovingdon Green	BV1	x	x					
Bradenham Puddingstone, north-west London Basin	3. The Coppice Bradenham	BD1	x	x					
		BD2	x	x	x	x	x	x	x
Alton, western Weald	4. Brightstone Lane	P1	x	x					
		P2	x	x					
	5. Bramdean	BR1	x	x			x	x	
		BR2	x						
South Downs, southern Weald	6. Goldstone Valley	GS1	x	x					
		GS2	x	x	x	x			x
	7. Chyngton	CH1	x	x					
	8. Seaford Head	SH1	x	x					

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Figure 1: Simplified geological map of southeast England with sampling locations and the approximate distribution of silcrete occurrences indicated. Silcrete distribution after White (1910), Brentnall (1946), Davies and Baines (1953), Bowen and Smith (1977) and Summerfield and Goudie (1980). Numbers refer to localities detailed in Table 1.

Figure 2: Example of a groundwater silcrete developed within a moderately well- to poorly-sorted inter-gravel sediment from The Coppice, Bradenham (sample BD2): (a) Sawn slab through the sample showing flint clasts and caps. Positions of cap structures are indicated by dashed lines; (b) Optical photomicrograph showing characteristics of silcrete matrix away from caps. Note well-defined optically-continuous quartz overgrowth cement throughout section. (c) Optical photomicrograph showing characteristics of silcrete matrix within a cap. The matrix comprises silt-sized quartz fragments within a microquartz and cryptocrystalline silica cement.

Figure 3: Example of a groundwater silcrete developed within a moderately well- to poorly-sorted inter-gravel sediment from Goldstone Valley, Hove (sample GS2): (a) Sawn slab through the sample showing flint clasts, caps and evidence of ferruginisation of the silcrete fabric. Prominent cap structures are indicated by dashed lines; (b) Optical photomicrograph showing well-developed optically-continuous quartz overgrowth cement in areas of the silcrete matrix away from caps. (c) Optical photomicrograph showing characteristics of silcrete matrix within a cap. Note the much poorer sorting of the host sediment, fretted edges of some quartz grains and dominance of microquartz and cryptocrystalline silica cement.

Figure 4: Example of a groundwater silcrete developed within poorly- to very poorly-sorted inter-gravel sediment from Brightstone Lane, Farringdon (sample P2): (a) Sawn slab through the sample showing flint clasts and caps (indicated by dashed lines); (b) Optical photomicrograph showing characteristics of silcrete matrix away from caps. Note the mixture of optically-continuous quartz overgrowth and microquartz cements; (c) Optical photomicrograph showing characteristics of silcrete matrix within a cap directly above the boundary with a flint clast (bottom left). Note the very poorly sorted host sediment cemented by cryptocrystalline silica.

Figure 5: Example of a groundwater silcrete developed within poorly- to very poorly-sorted inter-gravel sediment from Seaford Head (sample SH1): (a) Sawn slab through the sample showing flint clasts and areas of brown-stained way-up orientated cement; (b) Optical photomicrograph showing characteristics of silcrete matrix away from caps with well-developed optically-continuous quartz overgrowth cement.; (c) Optical photomicrograph showing characteristics of silcrete matrix within a cap directly above the boundary with a flint clast (bottom left). Note the very poorly sorted host sediment and opaque cryptocrystalline silica cement.

Figure 6: Example of a groundwater silcrete developed within poorly- to very poorly-sorted inter-gravel sediment from Ley Hill, Chesham (sample LY2): (a) Sawn slab through the sample showing flint clasts and caps (indicated with dashed lines). The box indicates the position of optical photomicrographs; (b) and (c) Photomicrograph showing an almost entire cap developed above a flint shard (in plain- [b] and cross-polarised [c] light). Note the lack of sand-sized particles within the lower part of the cap and the pervasive dark colour of the matrix in comparison with the surrounding fabric.

Figure 7: Poorly developed cusplate feature (arrowed) defined by Ti-rich grains developed within silcrete lacking optically continuous quartz overgrowths (sample LY2, Ley Hill).

Figure 8: Colour-CL images of a transect through a cap (sample BD2, Bradenham): (a) Base of the cap closest to the flint clast (bottom left hand corner). The host sediment comprises (i) sand-sized angular to sub-rounded quartz fragments (some with whole or partial inherited overgrowths) of high and low temperature origin indicated by the range of colours from blue to red, and (ii) silt-sized quartz fragments between these grains. The silcrete is cemented by cryptocrystalline silica; (b) Midway through the cap. The host sediments exhibit the same mixed provenance and cement but more intermediate sand/silt sized material is present; (c) Upper edge of cap at the boundary (dashed line) with the surrounding optically-continuous quartz overgrowth cement. The cap comprises cryptocrystalline silica cemented sand- and silt-sized quartz whilst the quartz overgrowth cement (arrowed) has a much lower silt content; (d) Optically-continuous quartz overgrowth fabric (arrowed) away from the cap. The host sediment is much better sorted and lacks silt-sized fragments.

Figure 9: The boundary between a cap (left side of images) and the overlying optically-continuous quartz overgrowth fabric (right side), sample GS2, Goldstone Valley: (a) Colour-CL image in which the contrast in host sediment and cement characteristics is clearly displayed. Quartz host sediment grains are more poorly sorted and of a smaller size within the cap. Cryptocrystalline silica and microquartz cements dominate the cap fabric, whilst the overlying fabric is cemented by angular quartz overgrowths. There is a clear difference in porosity (resin in pore spaces luminesces green), with dissolution of the silcrete fabric (cement and grains) focused along the boundary between the two fabric types; (b) BSE image from a different area of the same sample. Opaque minerals (light coloured) are more abundant within the cap and the difference in porosity is particularly evident.

Figure 10: EDS line analyses showing variations in Al and Ti along an 8mm transect through a cap structure (sample LY6, Ley Hill).

Figure 11: Ti elemental map from sample LY2 (Ley Hill). Ti is present throughout the silcrete matrix but with accumulations on the upper surface of flint and other detrital clasts. The majority of Ti-rich particles are cryptocrystalline ($<1\ \mu\text{m}$) but there are also larger (up to $40\ \mu\text{m}$) grains present. Note the absence of any Ti-rich laminations within the silcrete.