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The Petrography and Origin of Deposits filling Solution Pipes in the Chalk near South Mimms, Hertfordshire

J. THOREZ, P. BULLOCK, J. A. CATT & A. H. WEIR

Summary. Pipes and other solution cavities in the Upper Chalk near South Mimms contain deposits unlike those found in similar situations elsewhere in Great Britain. The cavities were formed near the sub-Palaeogene surface, and most of the deposits in them were derived from the basal Palaeogene beds (Thanetian and Sparnacian). A dark brown and very porous clay, which lines many of the pipes, is composed partly of the insoluble residue from the Chalk and partly of clay eluviated from the Palaeogene deposits. The clay was deposited from percolating water in spaces formed by dissolution of chalk at the margins of the pipes.

1. Introduction

Deposits immediately overlying the Chalk and filling solution cavities in it have been studied petrographically in Great Britain by Avery *et al.* (1959), Hodgson, Catt & Weir (1967) and others; this work has proved useful in tracing the origin and development of superficial deposits, which constitute many of the chalkland soils. The chalk quarry at Castle Lime Works (National Grid Reference: TL 230025) near South Mimms (Herts.), approximately 25 km NNW of central London, exposes many pipes and solution hollows filled with clay, loam and sand. These, deposits differ from the Clay-with-flints that is usually found in comparable situations elsewhere in south-east England, and therefore deserve special attention. Three main types of structure can be recognized in the quarry:

(a) basins, 1–3 m deep and up to 30 m wide, which occur beneath the thin (1–2 m) overburden of red-brown stony clay soil, and contain the flint-rich, glauconitic Bullhead Bed overlain by light grey (10 YR 7/2) and strong brown (7.5 YR 5/6) pebbly sands with clay partings (Colour descriptions are taken from Munsell Color Charts);

(b) vertical or steeply inclined cylindrical pipes, 0.5–5 m wide, which commonly penetrate the chalk to depths of 12 m or more, are filled usually with light grey and brown pebbly sand, and are lined with dark brown (7.5 YR 3/2 and 7.5 YR 4/4) clay;

(c) horizontal seams, up to 0.5 m thick, of dark brown clay and light grey sand (the sheet pipes of Kirkaldy, 1950), which occur mainly near the lowest level of the quarry at 12–20 m below the ground surface.

2. Material studied

We studied the mineralogical composition and micromorphology of the main types of deposits in the pipes by selecting samples from a large vertical pipe near the south-west corner of the quarry (samples A–M, Fig. 1) and a basin on the western side (samples X–Z, Fig. 2). The large vertical pipe contains a greater

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variety of deposits than most of the smaller pipes exposed in the quarry, but is lined with the same dark brown clay. At least three similar large pipes containing mottled sands and flint-containing loams are exposed in the quarry at present, but there are twenty or more small vertical pipes filled with unmottled light grey sands. In some pipes the brown clay lining contains small chalk fragments, and in others this clay is almost black; yet others contain reddish-yellow (7.5 YR 7/8) and brown (7.5 YR 5/6) accumulations of almost pure ferric oxide.

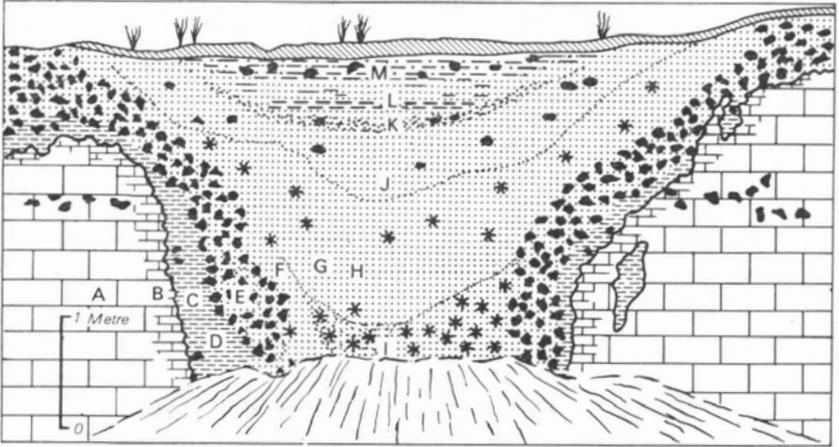


Figure 1. Section of large vertical pipe in south-western part of Castle Lime Works chalk quarry near South Mimms, Hertfordshire. A. Unweathered chalk. B. Chalk weathered into small angular blocks, separated by thin impersistent strands of dark brown (7.5 YR 4/4) clay. C. Very porous dark brown (7.5 YR 3/2 and 7.5 YR 4/4) slightly black-stained clay, containing many unworn, but often fractured, white-coated flints. D. Similar to C, but less porous and more black-stained. E. Brown iron-stained sandy clay loam, containing abundant fractured green-coated black flint nodules and black flint pebbles. F. Light yellowish brown (10 YR 6/4) sand, with a few black mottles and a few flint and quartzite pebbles. G. Yellowish brown (10 YR 5/6) loamy sand, with common black mottles and a few flint and quartzite pebbles. H. Yellowish brown loamy sand, with a few black and rusty mottles and a few pebbles. I. Dark brown sandy loam, with extremely abundant black mottles and a few pebbles. J. Light grey (10 YR 7/2) loamy sand, with common rusty mottles and a few flints and quartzite pebbles or angular fragments. K. Light yellowish brown (10 YR 6/4) loamy sand, with common rusty mottles and a few flint fragments. L. Pale brown (10 YR 6/3) sandy clay loam, with a few thin horizontal clay partings. M. Light yellowish brown (10 YR 6/4) sandy clay loam, with well-developed angular blocky structure and a few flint fragments.

The deposits in the basin (Fig. 2) are the lowest 1–2 m of the Palaeogene succession; they are only slightly disturbed and probably lie not far below the original sub-Palaeogene surface, because Sparnacian deposits (Reading Beds) occur *in situ* on the slightly higher ground immediately west of the quarry. However, superficial disturbance and possibly also some dissolution of the chalk are indicated at the margin of the basin, where the chalk rises steeply and locally even overhangs the basin deposits.

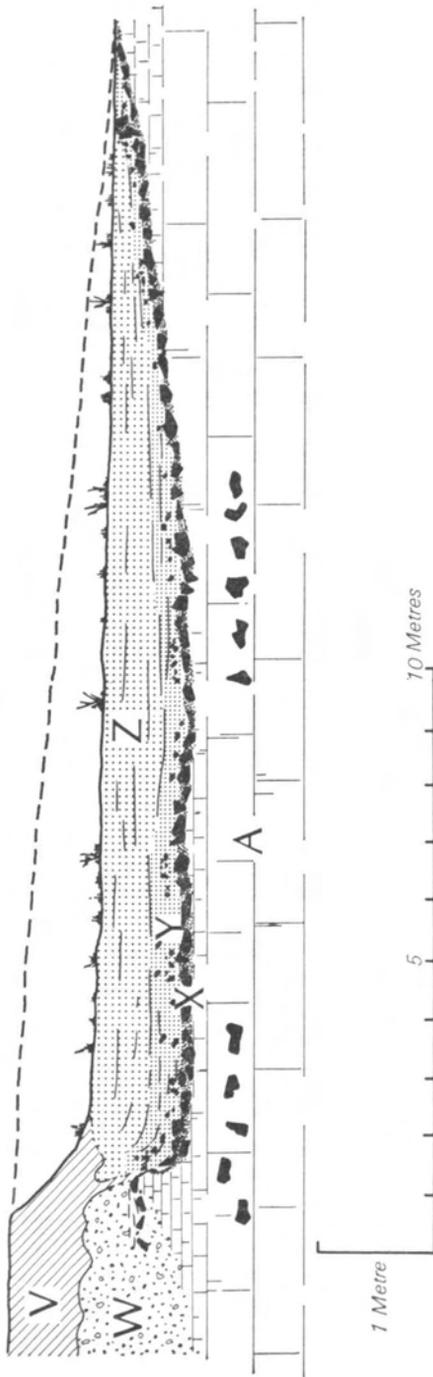


Figure 2. Section of broad shallow basin in north-western part of Castle Lime Works chalk quarry. A. Unweathered chalk. V. Red-brown stony clay soil. W. Chalk rubble. X. Brown iron-stained sandy clay loam, containing abundant fractured green coated, black flint nodules and flint pebbles. Y. Light grey (10 YR 7/2) and strong brown (7.5 YR 5/6) sands with clay partings and many black flint pebbles. Z. Strong brown sands with clay partings.

3. Analytical methods

Thin sections of the deposits were cut from blocks impregnated with Autoplax 110 resin and embedded in Ceemar FR264 resin. The particle size distribution of the samples was determined by the pipette sampling technique, and fine sand (50–250 μm) and clay (<2 μm) fractions were separated from the samples by sieving and repeated settling in dilute suspension. The fine sands were divided into light and heavy fractions with bromoform, and analysed mineralogically with a petrological microscope. The clay fractions were analysed by X-ray diffractometry of oriented aggregates and lightly compressed powders, and relative amounts of layer silicate minerals, jarosite and quartz were calculated from their reflection intensities. Apatite was estimated from total phosphorus, determined chemically, and iron oxides were estimated by the dithionite extraction method of Aguilera & Jackson (1953). The morphology of clay particles was studied with an electron microscope. As the deposits filling the pipes and hollows possibly contain some natural insoluble residue from the chalk, a large sample (approximately 700 g) of clean chalk from the quarry was treated with 2% acetic acid, and the clay and fine sand fractions of the insoluble residue were analysed mineralogically.

4. Results

4.a. Mineralogy

The clay fraction from the acetic acid-insoluble residue of the chalk sample was 0.9% by weight of the original chalk, and contained 60% montmorillonite, in laths forming stellate aggregates similar to those described by Weir & Catt (1965), 25% mica, 6% apatite, and a little quartz. The fine sand fraction was composed mainly of flint fragments, but also contained small amounts of collophane, similar to that described by Brown & Ollier (1956), limonite, siderite, glauconite, detrital quartz and alkali feldspar, and black or dark brown ferri-manganiferous concretions. The glauconite forms greenish yellow, sub-spherical, microcrystalline aggregates, with mean refractive index near 1.615; X-ray powder diffractometry shows that these are composed mainly of mica with some interstratified expanding layer silicates and a little quartz.

Table 1 shows the particle size distribution of the deposits in the large vertical pipe and the shallow basin. The Bullhead Bed in the shallow basin (bed X) is a mixture of green-coated black flint nodules and pebbles, sand of similar mineralogical composition to that of the Thanet Beds elsewhere in south-east England (Weir & Catt, 1969), and clay similar to that from the insoluble residue of the chalk. The clay contains 32% apatite and 15% iron oxides (mainly goethite), but the layer silicate minerals are exactly like those in the chalk. The basin deposits (beds Y and Z) overlying the Bullhead Bed also contain sands that are mineralogically similar to the Thanet Beds. The small amounts of clay that they contain differ from the clay in the chalk and Bullhead Bed in containing a little kaolinite (<5% in bed Y and about 10% in Z), but no apatite, and a montmorillonite that forms mainly anhedral flakes. Among English Palaeogene sediments, this clay seems to be transitional between that typical of the Thanet Beds,

which has no kaolinite (Weir & Catt, 1969), and that of the Reading Beds, which contains 20% kaolinite (Hodgson *et al.* 1967).

The dark brown clay lining the large vertical pipe (beds C and D) has an unusually low bulk density (undisturbed dry density of 1.0 g cm^{-3} at a moisture content of 21%), and feels very light in hand specimen, but contains as much as 81% clay (Table 1). Its $<2 \mu\text{m}$ clay fraction contains 60% montmorillonite in small anhedral flakes, 20% mica, 10% kaolinite, and small amounts of apatite, quartz, goethite and lepidocrocite. Only a small part of this clay could therefore have been derived from the chalk. In contrast, its coarser fractions are almost entirely chalk-derived. The flint nodules in it (Fig. 1) are white-coated and unworn, and resemble those in the adjacent chalk, and the sand fraction is composed of flint fragments, colophonite, chalcedony similar to that replacing chalk fossils (Brown *et al.* 1969), and small amounts of limonite, siderite, glauconite, quartz and alkali feldspar. The sand also contains the black or dark brown ferrimanganiferous concretions that are common in the insoluble residue of the chalk. Partial chemical analysis of a sample of these concretions, separated electromagnetically from the sand of sample C, showed that they consist mainly of iron and manganese, with some silica and alumina (probably in included clay) and organic matter.

The flint-rich bed (bed E) in the vertical pipe strongly resembles the Bullhead Bed (bed X), both lithologically and mineralogically. The flint nodules and pebbles in the two beds are similar in size, shape and abundance, and the sandy clay loam matrix of both beds has a similar particle size distribution (Table 1). The fine sand of bed E resembles that of the Thanet Beds, but also contains many jarosite aggregates. The clay contains 60% montmorillonite, most of which is morphologically similar to that in the chalk, 15% mica, 15% iron oxides (goethite and lepidocrocite), 3% apatite, 5% jarosite, and traces of kaolinite and quartz.

The fine sand fractions of beds F, G and I contain small amounts of jarosite and ferrimanganiferous concretions, but otherwise resemble those of the Thanet Beds. The small amounts of clay in these beds are mineralogically similar to those in the basin sediments (Y and Z): in particular they show the same increase in kaolinite away from bed E as Y and Z do from the Bullhead Bed (X). The clay fractions of beds J, K, L and M contain 55% montmorillonite, 25% mica and 20% kaolinite; this is similar to the composition of clay from the Reading Beds (Hodgson *et al.* 1967). However, the fine sands of these beds are more variable in origin. In bed L the heavy sand minerals consist only of iron oxides, zircon, tourmaline, rutile, staurolite and kyanite; this assemblage is more restricted than those of the marine Palaeogene sediments in England, but matches that of the non-marine Reading Beds. The heavy fractions from beds J, K and M are composed mainly of the same minerals, but also contain small amounts of epidote, zoisite, anatase, brookite, garnet, hornblende and andalusite. These additional minerals may reflect the incorporation of small amounts of material from either marine Palaeogene sediments or local Pleistocene deposits.

4.b. Micromorphology

Thin sections of chalk from near the edge of the vertical pipe (Fig. 1) show

E

Table 1. Particle size distribution by weight percent of deposits filling a large vertical pipe and a shallow basin in the upper Chalk at Castle Lime Works, South Mimms, Hertfordshire (excluding stones > 2 mm). Figure 1 shows the location of samples C–M, Figure 2 the location of samples X–Z.

	C	D	E	F	G	I	J	K	L	M	X	Y	Z
Coarse sand, 250–2,000 μm	0.3	1.4	24.6	17.8	15.0	12.7	16.5	15.5	8.9	10.2	22.1	10.8	10.1
Fine sand, 50–250 μm	6.5	19.8	26.8	65.0	57.0	50.8	59.0	55.2	40.4	46.3	22.7	63.4	61.4
Coarse silt, 20–50 μm	2.2	6.6	5.8	2.2	7.5	7.8	5.8	6.2	10.8	9.3	6.7	3.7	6.9
Medium silt, 5–20 μm	4.3	8.0	6.6	1.9	7.1	8.8	5.6	6.1	11.2	8.2	7.0	2.8	2.4
Fine silt, 2–5 μm	4.3	5.3	4.3	1.9	2.0	3.3	1.3	1.1	2.6	2.7	6.0	2.0	1.6
Clay, < 2 μm	81.0	58.7	31.4	9.4	11.1	14.7	10.6	15.1	26.0	21.9	34.4	16.2	16.3
Total	98.6	99.8	99.5	98.2	99.7	98.1	98.8	99.2	99.9	98.6	98.9	98.9	98.7

ferrimanganiferous concretions embedded in solid chalk and increasing in abundance towards the pipe; many of them have a crude spherulitic structure. At the edge of the pipe (sample B) the chalk is very porous, with many fracture planes widened by dissolution into channels of variable width, and subspherical pores approximately $50\ \mu\text{m}$ across. The channels and pores are lined or filled with strongly oriented, laminated clay (argillans), which is yellow-brown and moderately pleochroic. The strong orientation results from the deposition of platy clay particles from suspension in percolating water that had carried them down from overlying deposits (Stephen, 1960).

The dark brown clay lining the pipe (bed C) is also very porous, and this accounts for its small bulk density. However, it has few channels, and most of its pores, which occupy up to 40% by area at the edge of the pipe, are irregular equant or irregular prolate. Most of the clay occurs either in randomly distributed weakly oriented patches (argillasepic fabric of Brewer, 1964, p. 310), or in un-oriented and almost isotropic patches. As much as 40% of the area of both these patches is occupied by ferrimanganiferous concretions about $40\ \mu\text{m}$ across, which are commonly aggregated into secondary units up to $200\ \mu\text{m}$ across. The clay between the concretions is strongly impregnated with granules, $1\text{--}2\ \mu\text{m}$ across, of material similar in appearance to the concretions, and the weak birefringence shown by these parts of the clay probably results from disorientation caused by formation of the granules. Every void in this deposit is lined with laminated, strongly oriented and moderately birefringent clay, which resembles that lining the pores and channels in the adjacent chalk, except that it is less pleochroic and contains a few ferrimanganiferous granules and concretions. The pore space of the clay decreases away from the chalk junction, and patches of laminated and strongly oriented clay unassociated with present voids become common. We think that these are earlier void argillans, which have been embedded in the clay matrix by reorganization of the deposit, but have not yet been disoriented by impregnation with ferrimanganiferous material.

The flint-rich bed (E) has many voids lined with strongly oriented clay and also many embedded void argillans. The green coatings on many of the flints are composed of microcrystalline material resembling glauconite; it is similar in microscopic appearance to the glauconite that forms sand-sized pellets in the chalk, but is darker green and has a slightly greater refractive index (approximately 1.620). It is not sharply separated from the flint, but merges into it gradually over a pale green transition zone up to $300\ \mu\text{m}$ wide. This zone and the colourless unaltered flint are commonly separated by a narrow band of brown, iron-stained flint. The outer layers of the glauconite coatings are composed of larger crystals than the inner layers near the flint, and the material mixed with the quartz microcrystals in the pale green transition zone is extremely fine grained (probably $<1\ \mu\text{m}$). Moderately well crystallized glauconite penetrates narrow fissures and also occurs as isolated patches in both the green transition zone and the unaltered flint; it also partly replaces the silica of microfossils preserved near the margins of the flints. These features, which suggest that the glauconite coatings formed at least partly by reaction between the surface layers of flint and solutions penetrating these layers, occur also in the green-coated flints of the Bullhead Bed (bed X) at the base of the shallow basin.

The overlying sandy loam (beds F and I) is prominently mottled with ferri-manganiferous material similar to that in bed E. This forms dense patches, 1–3 mm across, which enclose sand grains and occupy up to 60% by area in thin section. Between these patches there is little fine material to separate the quartz sand grains, and most of the voids result from contact packing of these grains. There are a few thin channel argillans and thin free-grain argillans (layers of oriented clay surrounding and bridging sand grains), but the total amount of oriented clay is small. Samples G and H from the succeeding horizon have even less oriented clay. The rusty mottles in this bed are seen in thin section as iron-enriched nodules separated by colourless sand largely devoid of iron.

The highest layers of the pipe-filling (beds J, K, L and M) differ micro-morphologically from the deposits below (F, G, H and I) in several ways. They are much more heterogeneous in that they contain pockets of fine-grained material separated by coarser sediment; this heterogeneity increases towards the ground surface. They have fewer contact packing voids, and most of the pore space is attributable to channels and irregular equant or irregular prolate voids. They contain much more oriented clay, and void, free grain and embedded argillans are all common. Finally, mottling is less distinct and there are fewer dense, iron-enriched nodules.

5. Discussion

The mineralogical composition of the deposits in the pipes and solution hollows at Castle Lime Works indicates that they were mainly derived from Palaeogene sediments overlying the Chalk. The lowest 1–2 m of these beds are mineralogically similar to the Thanet Beds of Kent. From borehole evidence in north London Bromehead (1925, p. 14) suggested that the Thanet Beds thin out at depth near Hendon and Southgate, 9–12 km to the south-east. However, the zero isopachyte for the Thanet Beds should be drawn through or west of the quarry; the tentative line on Hester's map (1965, Fig. 7) seems on this evidence to be accurately positioned at this point. The thin Thanet Beds are overlain by multi-coloured clays (the Reading Beds), and these in turn by the grey London Clay.

Wooldridge & Kirkaldy (1937) suggested that the Mimms Valley, in which Castle Lime Works is situated, was cut originally during the Pleistocene by a temporary loop of the glacially diverted River Thames, which breached a gently domed cover of Palaeogene sediments but was then soon redirected to the south. The present misfit stream, the Mimms Brook, has subsequently enlarged the valley only slightly, so that the exposed chalk has been weathered for a long time by percolating rainwater, but has undergone very little surface erosion. The weathering is more intense near the edge of the Palaeogene outcrop than elsewhere, because above the thin sandy Thanet Beds the deposits covering the Chalk are essentially impervious clays, and surface water runs off them to enter the Chalk at their margin. Also, as a result of an anticlinal structure in the Chalk near South Mimms, the local water table in the Chalk is unusually far (at least 30 m) below the sub-Palaeogene surface, and this encourages rapid percolation.

Most of the material filling the solution cavities is pebbly sand similar to the Thanet Beds. The chalk therefore dissolves, at least initially, beneath a cover

of Thanet sands, which are then washed down into the cavities. While the Bullhead Bed at the base of the Thanet Beds remains coherent, it supports the sand, but the enlargement of the cavities eventually causes it to collapse, and the overlying deposits then fall bodily into the cavity. Such collapse evidently occurred in the large vertical pipe (Fig. 1), in which a disrupted Bullhead Bed (bed E) has fallen at least 3 m below the original sub-Palaeogene surface. Some of the overlying sands (beds F, G, H and I) are mineralogically similar to the Thanet Beds, and must have collapsed with the Bullhead Bed, but their appearance in the field has been changed by intense gleying, which caused both the black and the rusty mottling. The heterogeneous texture, microfabric and sand mineralogy of the highest beds in this pipe (beds J, K, L and M) suggest they are colluvial or solifluction deposits filling the surface depression that would have formed over the solution cavity after collapse of the sandy cover.

The dark brown, porous clay lining the pipes has a more complex origin, and one that is closely related to the mechanism of dissolution of the chalk. The flints and fine sand in it are derived from the chalk, but it is not a pure chalk residuum, because most of its clay differs mineralogically and morphologically from that in the chalk. Much of the clay is strongly oriented and laminated, and almost all of it would probably be the same if some had not been disoriented by formation of ferrimanganiferous granules. Strong orientation and lamination indicate deposition of the clay from suspension in percolating groundwater, so that most of the clay was probably derived from the overlying Palaeogene deposits and soils on them. Its mineralogical composition supports this suggestion.

The clay filling pores and channels in the weathered chalk near the edge of the vertical pipe is also mainly illuvial, because it is strongly oriented and laminated. A little of this clay might have been derived from the chalk, but the amount of chalk dissolved during formation of the channels and pores would obviously not provide enough clay to fill the same voids. As more space was provided by dissolution of chalk, more clay was deposited from the groundwater to fill the cavities. The blocks of chalk between the clay-filled channels thus slowly became smaller, and were eventually sealed in by encompassing layers of clay. The final removal of these chalk fragments was accomplished by slow diffusion of ions through the clay. However, at this stage further deposition of clay in the space provided by dissolution of chalk would be impossible, so that voids were left as the remaining chalk was dissolved. This accounts for the unusually large pore space and low bulk density of the fully decalcified clay.

Small chalk fragments remain incompletely dissolved in the clay lining of some pipes in the quarry, and other stages in the replacement of chalk by re-deposited clay are seen in the 'stoping' effects described in this quarry by Kirkaldy (1950). These effects are associated with the 'sheet pipes', which occur at greater depths in the chalk than most of the vertical pipes, and contain only illuvial clay and fine sand derived from the Thanet Beds. These materials were carried down through narrow fissures in the chalk by percolating water. Dissolution of chalk and redeposition of the clay and sand at depth probably occurred near the water table, so that the 'sheet pipes' possibly represent past water table levels in the chalk.

Some of the ferrimanganiferous concretions in the dark brown clay lining

the pipes probably came from the chalk as part of its natural insoluble residue. They occur in solid, unweathered chalk near the pipe and elsewhere in the quarry, and probably formed authigenically. However, much of the ferrimanganiferous material in other parts of the pipes (e.g. beds F, G, H and I) was not so derived, because these deposits contain little or no other chalk residue. Also, it is improbable that the small ferrimanganiferous granules impregnating much of the clay in beds C and D are derived unaltered from the chalk. Almost all the manganese and some of the iron in these deposits was probably derived in solution from waterlogged soils, and then concentrated by precipitation within the pipe. Drainage through some of the pipes must have been impeded at times, either by the clay bed adjacent to the chalk or by permafrost, and slow evaporation of the water and microbiological activity within it would have precipitated iron and manganese oxides. The increase in pH towards the chalk junction would also encourage such precipitation, especially in the clay lining the pipes. The ochreous deposits of iron oxide in some of the pipes possibly originated in similar ways, and the relatively large amount of iron oxide in the Bullhead Bed was probably also precipitated from groundwater by the increase in pH at the chalk junction. Some dissolved iron brought into the large vertical pipe was deposited there as jarosite; the sulphate ions necessary to form this mineral probably came from soils on the nearby London Clay, because the oxidation of pyrites in soils on the London Clay in Kent causes formation of jarosite (Weir & Catt, 1969, p. 32).

Our suggested origin of the dark brown clay lining the pipes is similar to that of the Beta horizons developed on calcareous gravels in Illinois (Bartelli & Odell, 1960). It is also similar to that of Clay-with-flints *sensu stricto* (Hodgson *et al.* 1967), which often occurs in similar situations, as a lining to pipes and other solution cavities. However, Clay-with-flints *s.s.* is redder (typically 5 YR 5/6), usually contains less ferrimanganiferous material, and has a higher bulk density. The clay we studied is darker mainly because it contains so much ferrimanganiferous material, and possibly also because it never underwent the long period of weathering in warm-temperate conditions that Avery *et al.* (1959, p. 192) suggested was important in the development of Clay-with-flints. The large pore space of the dark brown clay reflects its relatively recent formation, because the voids in Clay-with-flints have been gradually diminished by collapse, alternate swelling and shrinking, and slow continued deposition of further illuvial clay.

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