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Mineralisation of Shallow Fracture Surfaces in the
Chalk and Implications for contaminant attenuation

Paul Shand and John Bloomfield

Abstract

This report presents the results of a study of the mineralisation and micromorphology of shallow chalk fracture surfaces in the upper part of the Middle Chalk at Twyford Down, Hampshire. Samples were collected from recently exposed cuttings including (a) a vertical profile down to a depth of 7m and (b) within and adjacent to a complex fault zone approximately 15 m below ground level. The distribution and types of fracture minerals were studied in the field and selected samples were chosen for imaging using a Scanning Electron Microscope (SEM).

A wide range of fracture minerals were found on the fracture surfaces including Fe-rich clays, needle-fibre calcite and manganese spots. Illitic and montmorillonite clays were also present on fracture surfaces and detrital grains of quartz, barite and possibly gypsum were also noted. Manganese spots generally occur as isolated star shaped aggregates, but may from extensive precipitates on fault planes and on the surfaces of marl bands. Spongy-like textures and spherical interlocking platelets are considered to be early precipitates formed through bacterial mediation, which give rise with further precipitation to amorphous coatings. The Fe-rich clays are prominent at shallow depths, along major fault zones and associated with oxidised pyrite/marcasite nodules. They generally from extensive drapes completely covering the chalk and earlier manganese mineralisation on fracture surfaces. The development of the acicular needle-fibre calcite is related to precipitation from solutions supersaturated with respect to calcite. They are thought to have formed during formation of the zero-flux plane during the summer months or from rapid degassing of high pCO_2 soil derived waters. These form extensive crusts of calcite at depths of 3 to 3.5 m and represent the youngest mineralisation. Fracture mineralisation is considered to be important as indicators of hydraulically active fracture surfaces. The abundance and distribution of manganese spots on the surfaces of marl horizons is taken to be evidence for extensive horizontal fracture flow.

The abundant coatings on fracture surfaces are important in the retardation of solutes through the unsaturated zone and in the transfer of solutes between the pore and fracture waters. The iron and manganese phases are thought to essentially amorphous in character and thus may have extremely high surface reactivities. The development of abundant clays will also affect the flow of water between fracture and matrix, and even where matrix suction is high, the impermeable nature of fracture minerals may allow rapid transport through the unsaturated zone. These preliminary observations are likely to impose certain difficulties on models of solute transport through the unsaturated zone, particularly with regard to the heterogeneous nature of the mineralisation. The variation of fracture mineralisation both with depth and regionally is, however, poorly known and further work is required.

Acknowledgements

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1. Introduction

The Chalk aquifer is the most important public supply aquifer in the UK and displays the classic characteristics of a dual porosity aquifer. Chalk is a soft, microporous limestone of upper Cretaceous age, composed mainly of skeletal calcite (dominantly coccoliths) with minor amounts of other biogenic fragments. Although the Chalk is a relatively pure calcium carbonate, secondary mineralisation is generally conspicuous on fracture surfaces, however, this fracture surface mineralisation has been poorly studied. This report presents the results of a pilot study to characterise mineralisation on shallow fracture surfaces of the Middle Chalk at Twyford Down, Hampshire. The nature and degree of this mineralisation will be discussed in terms of the implications for geochemical processes and contaminant attenuation in the unsaturated zone of the Chalk aquifer. The micromorphology of the fracture surfaces was studied with the aid of a scanning electron microscope (SEM) and mineralogy was deduced through qualitative examination of emission spectra. The work was carried out as part of the National Groundwater Survey - Chalk Project, and was intended to complement parallel studies investigating regional trends in the matrix porosity of the chalk and laboratory studies of fracture surface chemistry. The following sections place the study in a wider hydrogeological context and show the scope and aims of the work.

1.1 Hydrogeological context

The chalk has been considered as a classic dual porosity aquifer with the matrix pores providing storage and the fractures providing areas of high permeability (Price et al., 1993). Porosity is generally high (typically 20 - 45 %), however, the small pore size (median < 1 µm) gives rise to low matrix permeability with solute movement taking place largely through molecular diffusion (Price et al., 1976). Although bulk movement of water is often considered to take place largely through advection in the fracture system, with large amounts of relatively immobile storage in the chalk matrix, there is still considerable debate as to the relative importance of flow which occurs through the matrix or fractures. Enhanced secondary permeability due to the development of fissures may also give rise to very high transmissivities (Banks et al., 1995; Younger & Elliot, 1995). Due to the relatively high overall permeability of the chalk, it displays only moderate to low head gradients. Consequently, in downland areas where there is significant topographic variation, the unsaturated zone varies from approximately zero in river valleys to more than 100 m over the interfluves (Price et al., 1993). Transmissivity values are generally highest along valleys and low under interfluves. Areas of enhanced fracture and fissure density are extremely important in the rapid transport of pollutants such as leachate from landfill sites through the unsaturated zone (e.g. Towler et al., 1985). Bath & Edmunds (1981) noted extensive fracturing down to depths of 40 m in a study of the Trunch borehole in Norfolk.

The carbonate matrix is dominantly composed of low-Mg calcite which is relatively stable at low temperature and pressure, therefore little recrystallisation has taken place, except at depths greater than 1000 m (Downing et al., 1993). An extensive open fracture-joint system has formed in response to uplift and later tectonic influences (Downing et al., 1993). The non-carbonate fraction of the chalk generally comprises clays but minor amounts of zeolite, quartz, collophane, dolomite, feldspar and barite have been noted (see Hancock, 1993 for summary). Original biogenic silica has undergone extensive diagenetic processes to form the typical 'flint' bands of the Chalk. Marl bands also occur, particularly in the Cenomian and Turonian, and in the

Cenomian of southern England may contain as much as 30 % clay (Hancock, 1993).

There have been a number of studies to characterise the distribution of hydrogeologically significant fractures in consolidated, relatively unweathered chalk (Woodward & Buckley, 1976; Patsoules & Cripps, 1990; Younger & Elliot, 1995), but little on the complex structures developed on fracture surfaces and in the weathered mantle immediately below the soil horizon. There are rapid changes in both the density and style of fracturing in the top few metres of the chalk (JPB reference), and carbonate dissolution and precipitation processes are likely to be important in modifying primary porosity and permeability adjacent to fractures (Bloomfield, 1994). The development of secondary mineral phases on shallow chalk fracture surfaces is generally very extensive and typified by clays and Fe and Mn sesquioxides. However, there has been relatively little work on the detailed chemistry and mineralogy, although the role of oxide coatings on fracture surfaces, as retardants to pollutant transport, has been documented in crystalline rocks (e.g. Casas et al., 1994; Landström & Tullborg, 1990). The surface properties of these fracture surfaces and the extent of secondary mineralisation affects both porosity and permeability and therefore are important controls for the diffusional interchange of dissolved solutes between fracture and matrix. The ability of iron and manganese hydroxides, clays and organic material to coprecipitate and/or scavenge trace metals is well established (Murray, 1975; Hem, 1977; Morel et al., 1973) and may have important consequences for element mobility in shallow aquifers. Controls on the precipitation of oxide/hydroxide phases in freshwater systems, particularly those of manganese are the subject of much debate, specifically the roles of physicochemical vs. biological processes (Nowlan et al., 1983; Robinson, 1993).

The transport of pesticides may be strongly affected by adsorption along fracture surfaces, and sorption onto clays (Lee et al., 1990; Laird et al., 1994) and organic substances (Landrum et al., 1984; McCarthy & Jimenez, 1985) is well established. Groundwater sources are also potentially at risk of contamination from three types of pathogens: protozoa eg. *Cryptosporidium* and *Giardia*; bacteria eg. *E Coli* and *Streptococcus*; and viruses (Carrington et al., 1989; Bryan & Pike, 1990). There is some evidence that pathogens can be sorbed onto the surface of clay minerals (Lewis et al., 1982; Gale, 1990). High concentrations of bacteria in bottom muds of rivers (Grimes, 1980) and enhanced survival in seawater experiments with estuarine sediments (Gerba & McLeod, 1976) highlight the importance of adsorption in controlling amounts. There is also an extensive literature describing the sorption of viruses onto clays such as kaolinite and montmorillonite (see Gale, 1990 for review). The distribution of bacteria in aquifers is unlikely to be uniform with greater numbers on fracture and fissure surfaces (Clark et al., 1991) and this will probably be enhanced in the chalk where extremely small pore-throat diameters are present in the chalk matrix (Price et al., 1976). The presence of bacteria and bacterial biofilms on fracture surfaces is important in terms of geochemical processes e.g. denitrification (Lawrence & Foster, 1986; Clark et al., 1991) and retardation of heavy metals (e.g. Nelson et al., 1995). Several studies have shown the presence of a wide range of bacteria in the unsaturated and saturated zones of the chalk (Towler et al., 1985; Clark et al., 1991).

Flow conditions and water chemistry are significant factors controlling the nature of mineralisation along fracture surfaces, and are briefly summarised in the following sections.

1.2 Flow in the unsaturated zone

The unsaturated zone of the Chalk is defined as the part of the aquifer that lies above the deepest

water table and is the zone in which the pore water pressure is less than atmospheric pressure (Price et al., 1993). However, much of this zone is often close to saturation. There have been numerous field studies of pore-water pressure variations and their relation to hydraulic conductivity, and sophisticated models developed to explain the field data. The degree to which bulk transport takes place through the chalk matrix or via fractures and conduits in the unsaturated zone of the Chalk has important implications for rates of transport and retardation of pollutants towards the saturated zone. Fracture flow is considered to be the dominant control on rapid transport through the unsaturated zone of the chalk due to the relatively large apertures of the fractures with respect to the microporous matrix (Wellings & Cooper, 1983; Foster, 1993). The degree to which recharge water is transmitted through the matrix or through fractures is, however, still intensively debated. Theoretical models of the hydraulic behaviour of water in the unsaturated zone have been developed, for example by Wellings & Bell (1982) and Wellings (1984), and reviewed by Price (1993). The following summary is based on these studies.

The theoretical relationship between elevation head, pressure head and water content in an ideal granular aquifer that is fully saturated is illustrated in Figures 1a and 1b. If it is assumed that the profile is at equilibrium i.e. total head across the profile is zero, the water table is at atmospheric pressure and there is no vertical movement; then the pressure head will be negative and will increase linearly with depth, therefore pore water content increases with depth Below the water table, the pores are totally saturated, with water content being equivalent to porosity. The capillary fringe, immediately above the water table, is also fully saturated but the water is at less than atmospheric pressure. The capillary fringe exists because the pore space does not begin to drain until the pressure falls below a critical value known as the air-entry pressure, corresponding to the pressure head (ψ_A). The air-entry pressure is more negative for fine-grained materials with small pore throat sizes. Chalk typically has a pore throat size of less than 1 µm (Price et al., 1976), and may support a capillary fringe of up to 30 metres. Price et al. (1993) suggest that fractures in the unsaturated zone may typically have apertures of more than 50 µm, and these would only support a capillary fringe of c. 0.6 metres. The profile illustrated in Figure 1c may, therefore, be more representative of the chalk that shown in Figure 1b. Theoretically, at equilibrium, the pore spaces of the matrix may be expected to be saturated to a height of c. 30 metres above the water table, whereas fractures will only be saturated to a height of c. 0.5 metres above the water table.

This idealised equilibrium condition is unlikely to be attained in nature due to the combined effects of recharge and evapotranspiration which affect both the pressure and total head profiles. When water lost through evapotranspiration exceeds the rate of recharge, water may move upwards through the profile. This creates a maximum head in the profile known as the zero-flux plane (ZFP, Figure 2) which, in the chalk, is developed in the early summer and initially moves rapidly down the profile (Wellings & Bell, 1980). Residual drainage occurs continuously below the ZFP, but there is an upward flux above the plane to satisfy evapotranspiration demand. Following complete wetting of the profile, drainage then occurs through the whole profile during the winter months (Figure 1). If evapotranspiration is significant and the depth to the water table is very shallow, it is feasible that the ZFP will reach the water table and water will be drawn upwards. This area above the ZFP shows the greatest variation in volumetric moisture fraction, but below this depth (about 3 m in the English Chalk) continuous flow generally occurs throughout the year.

The degree of recharge through matrix or fractures in the unsaturated zone is a function of the recharge rate and hydraulic conductivity of aquifer material. Where the pore water pressure is greater than the air-entry pressure for the chalk matrix, but less than the air-entry pressure for the fractures (assuming all fractures have the same aperture), the matrix pores will become saturated throughout the profile, but the fractures will be drained except just above the water table. The hydraulic conductivity in this case will be the same as the hydraulic conductivity of the saturated matrix and, therefore, the maximum infiltration rate that can occur without fracture flow is approximately equal to the matrix conductivity. If the hydraulic conductivity of the matrix is less than the average rate of recharge, pore water pressure will increase until it exceeds the air-entry pressure of the fractures. The fractures will then fill with water and become conductive. It has been suggested that water will not flow through fractures in the unsaturated zone of the chalk at pressure heads of less than 0.5 m of water (Cooper et al., 1990; Gardner et al. 1990). Below this pressure head, flow will only occur through the saturated matrix. The saturated conductivity of the chalk matrix (K_m) is approximately 3 to 5 x 10^{-3} md^{-1}, and when infiltration or recharge exceeds this threshold, the fracture system becomes transmissive. Price et al. (1993) note that the fracture system acts as a one way flow system, where fractures transmit water to the water table at times of high recharge, but will always be empty because of low pore water pressures, during low recharge.

The above summary assumes that all fractures are of a constant aperture with the same air-entry pressure. However, in nature there are likely to be a range of fracture apertures that vary with tectonic history, lithology, geomorphology, position across an interfluve, type of cover etc. Where a range of fracture apertures exist, the narrower fractures are expected to become water saturated and conductive before wider ones. High transmissivities beneath some river valleys have been related to fissure development related to periglacial conditions (Younger, 1989) and in extreme cases the chalk may show properties of karstic aquifer flow (Banks et al., 1995).

1.3 Solute transport and water chemistry in the unsaturated zone

The transport and exchange of solutes in the chalk matrix takes place largely through diffusion, even though water movement may be extremely slow. When fracture flow occurs, exchange of solutes between matrix pores and the fractures takes place, but advection and dispersion are the dominant controls on flow through the fracture network. Foster (1975) and Barker & Foster (1981) developed a model of coupled advection and aqueous diffusion to explain tritium concentration profiles in the unsaturated zone, and it has been postulated that similar processes explain the from of nitrate and pesticide profiles (Foster et al. 1982, 1991; Foster, 1993). This coupled advection/aqueous diffusion model was based on an idealised dual porosity system with discrete boundaries between fracture and matrix porosity, and diffusion coefficients typical of chalk matrix material were used. This exchange between mobile fracture water and matrix pore-water is important in the retardation of solutes through the aquifer. The heterogeneity within the chalk aquifer makes it likely that there is considerable spatial variation in transport mechanisms in the chalk. It is also likely that the mechanism of water movement is temporally variable depending on rainfall intensity and the antecedent moisture conditions (Geake & Foster, 1989).

The soil zone provides an important control on the chemistry of shallow waters in the chalk due to the high pCO$_2$ concentrations developed due to biological activity. The pCO$_2$ and extent to

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which the system remains open with respect to CO_2 is a major control on determining the evolution of waters in carbonate terranes. The CO_2 dissolves to produce carbonic acid (H_2CO_3) which reacts with the carbonate minerals. The kinetics of this reaction is very rapid and saturation is generally reached within the top few metres of the chalk. The pH of the soil zone overlying chalk is typically 7.5 - 8.3 (Price et al., 1993). Seasonal variations in pCO_2 occur in the top 2-3 m of the chalk where open system conditions exist. Pitman (1979), in a study of the Middle and Lower Chalk in Yorkshire, found that pCO_2 was at a maximum in chalk soils during the late summer months, and that the soil leachate was oversaturated with calcite because of the high pCO_2. Soil waters were, however, found to be undersaturated with calcite during the winter recharge period (Pitman, 1979). The processes of carbonate dissolution and precipitation are, therefore, expected to vary in accordance with these variations.

Several processes occur in the unsaturated zone which affect the pore-water chemistry including (a) evapotranspiration which may significantly concentrate solutes, (b) uptake of solutes by biomass, (c) dissolution of aquifer matrix minerals, (d) precipitation of minerals (e.g. calcite, clays, sesquioxides) and (e) ion-exchange reactions. The latter processes (c - e) may significantly modify both the character and reactivity of fracture surfaces. It has been found that enhanced porosity occurs to a depth of 1 - 1.5 mm along chalk fractures in the chalk, related to carbonate dissolution (Bloomfield, 1994). The diffusional interchange of solutes between fractures and pore-waters is likely to be significant in the unsaturated zone with the fracture surfaces being important loci for both dissolution and precipitation. This is a two way process with diffusional transport into as well as out of the chalk matrix. The dominance of diffusive or advective transport may also cause differences in alteration of fracture surfaces (Steefel & Lichtner, 1994).

Chemical changes continue downgradient in the saturated zone with incongruent dissolution of carbonates in response to freshwater diagenesis (leading to higher solute Mg/Ca and Sr), redox processes, ion exchange and residence time being important controls on water quality. Waters with relatively high salinity occur at depth and the increase in concentration with depth in the profiles is thought to relate to diffusional exchange with a residual connate water (Bath & Edmunds, 1981; Edmunds et al., 1987). In deeper parts of the aquifer, significant differences may exist between pore-waters and fracture water (Edmunds, 1973).

1.4 Scope and aims

This study reports an investigation of the micromorphology of chalk fracture surfaces using scanning electron microscopy (SEM). As part of the BGS "National Groundwater Survey: Chalk Study", fracture surfaces of chalk were collected from Twyford Down, Hampshire (NGR SU 485 270). Samples were collected from fresh chalk faces exposed during road construction. The chalk fracture surfaces used for this study were sub-samples from those used for geochemical analysis and fissure surface characterisation (work in prep.).

The purpose of this report is to provide an initial appraisal of the mineralisation and micromorphological features of shallow fracture surfaces in the chalk, and to use the results to infer controls on precipitation and provide a preliminary assessment of the effects of mineralisation on the transport and attenuation of contaminants in the shallow unsaturated zone.

The following specific aims have been identified:

i) to establish appropriate sampling and sample preparation procedures that do not affect delicate mineralisation features on the fracture surfaces,

ii) to assess the feasibility of using SEM to characterise the mineralisation and micromorphological features of mineral coatings on chalk fracture surfaces,

iii) to investigate trends in surface mineralisation as a function of depth through one vertical profile of the chalk and the development of mineralisation around one faulted zone,

iv) to establish constraints on the relative age and physical and chemical conditions of mineralisation,

v) to provide a preliminary assessment of the implications of observed fracture surface mineralisation for solute and contaminant transport in the shallow Chalk aquifer.

The geology and hydrogeology of the study site at Twyford Down, sampling strategy, sample preparation procedures and analytical methodology are described in section 2. Section 3 will provide detailed hand specimen descriptions and SEM images. The discussion section will examine the likely controls on fracture surface mineralisation and implications for physical and chemical processes in the shallow unsaturated zone. The possible effects of secondary mineralisation on contaminant behaviour will also be discussed and recommendations for further work given.

2. The Twyford Down Study

Twyford Down (NGR SU 485 270) is situated approximately three kilometres south-east of Winchester, Hampshire. The area of this study is a 1300 m long, 20 m wide NE-SW oriented cutting excavated as part of the M 30 extension. The sides of the cutting reach a maximum depth of 20 m and are separated by approximately 30 m. The site is situated on an interfluve east of the river Itchen (Figure 3) with a maximum elevation of 100 m aOD. A scarp slope is present to the north and towards the river Itchen to the west and a dip slope to the south. The section is inferred to be Middle Chalk, probably Turonian to Coniacian in age, as the New Pit beds are exposed at the norther end of the exposure, and the Seaford Chalk is present at the souther end of the exposure (** Mortimore *pers. comm.*). Groundwater levels are at approximately 30 to 40 m aOD, i.e. the thickness of the unsaturated is approximately 60 m. On the basis of the potentiometric surface illustrated on Figure 3, it is inferred that groundwater flow is predominantly to the south or south-west, however flow at the site may locally be directed towards the river Itchen to the west.

2.1 Site description

The soil at Twyford Down is a thin clayey soil up to 30 cm thick, typical of chalk downland. The junction between the soil and the weathered chalk mantle is abrupt and well defined. Adjacent to the soil horizon the chalk is typically rubbly in appearance. The sequence below the soil cover comprises off-white medium to thickly bedded chalk with flints and marl seams. Nodules of ferric oxides with radiating internal structure pseudomorphing pyrite or marcasite, were occasionally present in bands within the chalk. The principal structural features exposed are bedding plane fractures, joints and faults. The bedding is primarily defined by changes in matrix bulk density, marl bands and nodular flints and a general view of part of the cutting is shown in Plate 2.1. Bedding plane fractures are often laterally persistent, particularly those associated with marl bands. The chalk is pervasively jointed and has a blocky appearance, with blocks of the order of 10 to 30 cm being common and defined by regular to irregular planar joint surfaces. Joints generally are at a high angle with respect to bedding and are generally confined to single lithological units, but intensity may vary significantly between and along beds. Conjugate pairs of relatively large joints developed in the thicker units, and that cut across several units, may locally lead to wedge failure.

There is extensive faulting at the site, typically vertical or normal, which may be arranged in conjugate pairs. The normal faults typically dip to the south at angles in excess of 60 degrees. Many of these transect the entire face of the outcrop, however, it is often difficult to correlate faults across the cuttings. Displacements on the faults are generally very small, typically less than 50 cm (Plate 2.2), and spacings are on the scale of 20 to 100 m. Some of the larger faults are not single surfaces, but may in places comprise a complex zone of anastomosing faults. Some of the faults also contain fault gouges and breccias. There is also evidence for the development of hard, re-cemented chalk in the vicinity of some faults (Mortimore, *pers. comm.*) and dissolution cavities are also present.

Bedding plane fractures, joints and faults were often stained orange-brown (Plate 2.3). This was more intense, but not confined to shallower sections or areas where bands of pseudomorphed

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pyrite/marcasite nodules were present. These orange-brown precipitates were inferred in the field to be ferric hydroxides.

Some shallow fracture surfaces exhibited a light grey to powdery white surface and this was particularly enhanced at a depth of approximately 3 to 3.5 metres. This mineralisation covered both manganese spots and ferric hydroxides, thus representing the youngest mineralisation noted in the field.

Manganese mineralisation occurs as radial dendritic growths (plates 2.4 and 2.5) on most chalk fracture surfaces, and laterally persistent bedding plane fractures, marl bands and larger faults are often locally highly mineralised. The manganese "spots" were spatially independent of the iron staining, but where the two minerals occurred together, the manganese spots were always present beneath the ferric hydroxides and therefore older. Since the mineralogy of these dendrites is unknown at present, they will be referred to as manganese (hydr)oxides, however, it is likely that they are more likely to be poorly ordered amorphous manganese sesquioxides. Generally the dendrites occur at low density as isolated 'spots' which vary from less than 1 to 5 mm in diameter, but may locally completely cover the fracture surface of some fault planes (Plate 2.6). Field observations suggest that the distribution of manganese oxides on marl horizons is controlled by the microtopography of the fracture surface: where the bedding planes show undulating topography, manganese spots were found to be preferentially distributed on down-dip, steep faces on the fracture surface (Plate 2.7). Where marl horizons were traversed by vertical joints, splays of manganese (hydr)oxides are aligned vertically down the joint (Plate 2.8). Although slickensides and recrystallised surfaces were present in some of the fault zones, there was only one occurrence where the manganese oxides showed evidence of slickensiding.

2.2 Sampling strategy, preparation and SEM techniques

Two suites of samples were collected. The first was a vertical profile with samples collected at one metre intervals to a depth of seven metres below the soil zone. These were collected through a relatively unfaulted section of the exposure in order to study changes in fracture mineralisation with depth. Fracture surfaces showed variable orange-brown staining which was particularly intense in the shallowest zone. Manganese spots were present on fracture surfaces below the ferric hydroxides and on fresh surfaces at depth. Occasional plant roots were noted in the shallower parts of the section.

The second suite was collected from a fault zone at a depth of approximately 15 m below the soil zone. Samples were collected within the fault zone, unfaulted areas away from the fault zone and from marl bands on both sides of the fault Plate 2.2). The displacement of the marl bands across the fault indicate a maximum throw of approximately 50 cm. Abundant manganese oxides were present within the fault zone and also on the upper surfaces of the marl bands. Orange-brown staining was not as prominent as at the top of the vertical section, and was generally confined to areas spatially associated with a band of oxidised pyrite nodules.

One sample (Shoreford Road) of fresh soft white chalk was in addition collected from the southern end of the road cutting.

Samples were washed with deionised water to remove any loose debris, but not treated in any other way to avoid disruption of the surface. Small sub-samples (up to approximately 20 mm) were mounted on aluminium stubs and carbon coated. A Cambridge Stereoscan 250 Scanning Electron Microscope (SEM), run at 20 keV, was used in both normal and backscattered mode to study the fracture surfaces. Most of the SEM images presented in this report were obtained in normal SEM mode, and are comparable with images obtained in reflected light i.e. they show the topographic features of the fracture surface. The images obtained in backscattered mode are a function of the molecular mass of the phases at the fracture surface. Consequently, where there is a significant difference in molecular mass between two phases e.g. between calcite and manganese oxide, the backscattered image shows a strong contrast and the image highlights changes in chemical composition. Phases with higher molecular masses are relatively bright, and phases with lower masses are relatively dark.

3. Chalk fracture descriptions

The following sections describe the characteristics of the chalk fracture surfaces in hand specimen and under the SEM. The SEM descriptions are illustrated using photomicrographs taken from the Shoreford Road, vertical and faulted sections.

3.1 Shoreford Road section

The fracture surfaces at the Shoreford Road cutting showed relatively clean surfaces with abundant manganese spotting. The spots showed a random distribution, with individual spots forming star-like dendritic patterns. Although in most cases the Mn spots occurred on white chalk surfaces, some fractures were coated with an orangey brown material which looked like ferric hydroxides. Where this brown coating was thin occasional manganese spots were seen beneath the coating.

Under the SEM the surface was relatively clean and fresh with entire undeformed coccoliths (Plate 3.1), and with limited recrystallization of authigenic calcite. A lot of structural detail was preserved on the coccoliths implying very little recrystallization or dissolution has occurred and this was confirmed by occasional large complete foraminifera tests or gastropod shells. Subhedral barite (c. 15 x 5 µm) was found and also implies very little solution. Manganese spots were not seen on the surface with the SEM and there was no evidence of significant quantities of clays on the surface. It is therefore suspected that the surface studied was part of a freshly broken surface which had been carbon coated and not the true fracture surface.

3.2 Vertical section

The descriptions of the samples from the vertical section correspond with the SEM images shown in Plates 3.2 to 3.11. The photomicrographs were taken in normal SEM mode unless otherwise stated. Table 1 summarises the mineralisation down the depth profile.

3.2.1 1-2m sample

The fractures at 1.2 m exhibited extensive orange-brown staining, and in hand specimen were covered with a thin orange to thicker dark brown coating. This coating was sufficiently thick in places to mask the natural roughness of the fracture surface. A white crust is locally developed over parts of the fracture surface, and occasionally plant roots were seen to be enclosed within the crust.

Under the SEM, the chalk matrix was largely obscured by an amorphous looking phase that forms drapes or a veneer over the topography of the fracture surface (Plate 3.2). Qualitative spot analysis indicated that the amorphous phase is rich in iron, potassium and aluminium. It is inferred that the brown coatings are therefore iron-rich clays, but it not clear to what extent this could be due to entrapment of clays within ferric hydroxide. These will be classified as "Fe-rich clay" in this report, but further work is needed to confirm the true identity of the phase. The Fe-

rich veneer is extremely thin (a few microns) and occasional features of the chalk surface (e.g. coccoliths, Plate 3.3) could still be seen on the fracture surface.

Acicular calcite crystals, typically < 1μm in diameter and up to 10μm in length were present on the fracture surface on the Fe rich phase (Plates 3.2 and 3.3). These generally form single crystals, but occasionally form double rods comprising two parallel crystals were noted (Plate 3.3). The length:width ratios for these needles were typically of the order of 4:1 to 10:1. They are assumed to calcite, the most stable $CaCO_3$ polymorph under ambient conditions. The acicular calcite did not appear to show any preferred orientation but commonly formed clusters comprising parallel to sub-parallel crystals (Plate 3.3). Micritic calcite forming squat prisms were present in intimate association with the acicular forms (Plate 3.3). Some calcite crystals show rather diffuse edges and sometimes blend into structureless micritic calcite (Plate 3.3). Such features are probably due to partial recrystallisation of original acicular calcite by recharging soil-derived waters.

Large 20 - 30 μm open pores were present on the fracture surface, and may be associated with foraminifera or shelly porosity in the chalk matrix. It is known that foraminifera tests and some larger bioclasts may be susceptible to preferential carbonate dissolution due to slightly higher Mg substitution in the calcite (Scholle et al., 1983; Hancock, 1993).

A fresh broken surface, perpendicular to the fracture was also studied. No acicular calcite, clays or oxides were seen on the fresh broken surface. Pore sizes were typical for a white chalk ranging from less than 1 μm associated with the matrix, up to 30 μm associated with relatively large foraminifera. A single spot analysis showed that the chalk had a Ca:Mg ratio of 10:1. One grain was also noted with a S and Cl peak probably gypsum or anhydrite. A single detrital quartz grain was noted. The matrix beneath the mineralisation showed moderate recrystallization with some calcite rhombs in large pores after foraminifera, and there were few recognisable coccospheres. Manganese spots were not observed in hand specimen or under the SEM, but this may be due to masking by the amorphous Fe-rich phase.

3.2.2 3.0 m sample

The fractures at 3.0 m depth generally showed abundant orange-brown staining, which was covered with a white crust. The crust was seen under binocular microscope to comprise a mat of very fine-grained acicular crystals of calcite. The calcite also contained occasional thin plant roots, and in places the acicular crystals completely enclosed parts of the roots. Where these coatings were relatively thin, manganese spots could easily be distinguished beneath the calcite mat. One fracture was heavily orange stained with acicular calcite on the main fracture, but a smaller sub-parallel fracture, separated from the main fracture by approximately 5 mm, only exhibited manganese spot mineralisation.

The 3.0 m fracture surface, when analysed under the SEM, was almost entirely covered by a dense mat of interlocking acicular calcite (Plate 3.4), with subordinate patches of amorphous Fe-rich clay. Plate 3.5 illustrates a broken section through a natural fracture surface, with the coating of acicular calcite and clay on the right of the figure and the chalk matrix on the fresh broken face to the left of the figure. The surface mineralisation is approximately 20 to 30 μm thick, below which the chalk exhibits limited recrystallisation. The chalk beneath the acicular calcite coating

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was relatively fresh, with abundant coccolithic fragments (Plate 3.5).

The acicular calcite on the 3.0 m surfaces showed a broader range of aspect ratios than those found on the 1.2 m section. Maximum aspect ratios were significantly higher, at least in excess of 100:1. These are identical to acicular calcites presented elsewhere (Phillips & Self, 1987; Strong et al., 1992) but calcite with serrated edges (Phillips & Self, 1987) were not present. Small (1 - 2 µm) stubby prisms of micritic calcite were intimately associated with the acicular mat and on a partly exposed plant roots (Plate 3.6). The acicular calcite did not exhibit a single preferred orientation, but locally calcite showed strong parallel and sub-parallel alignment forming interlocking concentric arrays approximately 20 to 40 µm in diameter (right hand side of Plate 3.4). Large (up to several hundred µm), open pores were present in the calcite mats (Plate 3.7). The large pores show no evidence of erosion or dissolution, but the calcite crystals are tangentially arranged around the margins, often forming curved crystals (Plates 3.8 and 3.9). Curved crystals are were also present along the cuspate structures developed on the calcite mat (Plates 3.4 and 3.7), and although the controls on these structures are unknown it is likely that their development is in some way related to flow across the fracture during crystallisation, for example the flow in Plate 3.4 is inferred to be from left to right.

3.2.3 3.5 m sample

The samples from 3.5 m were very similar to the 3.0 m sample with acicular calcite developed over an Fe rich clay layer. The fracture surfaces were, however, variable with areas of less intense mineralisation dominated by manganese spots. Under the SEM acicular calcite development was identical to that at 3.0 m with curved tangential calcite developed around open pores (Plate 3.9). It is inferred that these structures may have developed over open pores present in the clay coatings (Plate 3.10), which themselves may have developed over the larger pores in the chalk matrix.

The orange-brown staining varied from pale orange with manganese spots visible below the staining to opaque dark brown clays. Viewed through the binocular microscope the Fe-rich coatings appear as orangey-brown amorphous looking botryoidal coatings draped over the chalk surface. Manganese spots were present over much of the fracture surfaces, but generally much better developed and thicker in hollows on the surface. Under the SEM the fracture surfaces were almost entirely obscured by Fe-rich clays (Plate 3.10). The clays were draped over the fracture topography smoothing the fracture surface. Occasional pores were present in the clay coating approximately 10 to 20 µm in diameter (Plate 3.10), but it was not possible to recognise the underlying features of the chalk matrix. Typical qualitative spot analysis showed strong Ca and Si peaks with less dominant Al and Fe. It was not clear to what extent the matrix adjacent to the fractures has been recrystallised as the clay coatings were sufficiently thick to obscure the matrix.

3.2.4 5.0 m sample

In hand specimen the 5.0 m fracture surfaces showed little mineralisation in comparison with the shallower fractures. Manganese spots were present and a limited development of Fe-rich clays. Under the SEM foraminifera and coccolithic fragments were readily visible, there was only

limited Fe-rich clay and acicular calcite was absent. Despite the absence of clays on the fracture surface, manganese spots were difficult to distinguish in normal SEM mode due to lack of contrast (Plate 3.11), but were very apparent in backscattered mode. The manganese spots were comprised botryoidal masses, approximately 50 to 100 μm in diameter. Qualitative analysis of the manganese spot on Plate 3.11 indicated that approximately 5-10 % Fe, 5% Co, 2-3% Ni and significant Ca and Zn were present.

3.2.5 6.0 m sample

Fracture surfaces from 6.0 m showed a variable degree of orange staining. Manganese spots were present both below the staining and on unstained fracture surfaces. Under SEM thin drapings of Fe-rich clay were present, but variable, on the fracture surfaces. Where the clay coating was relatively thin, recrystallised coccoliths and foraminifera tests were seen indicating relatively little matric dissolution. Due to inadequate carbon coating of the samples, images were poor and no photomicrographs were obtained.

3.2.6 7.0 m sample

In hand specimen, the 7.0 m fracture surfaces were similar to those at 6.0 m, with some development of Fe-rich coatings and manganese spots. Some fracture surfaces, however, were distinctly grey particularly in hollows in the fracture, in contrast to the white colour typical of the chalk. These surfaces under magnification were characterised by a smooth vitreous looking coating. Manganese spots were present but more dispersed than higher up the succession and a single, probably detrital, apatite grain was also noted.

3.3 Faulted section

Samples collected from this locality were chosen to be representative of a complex area within and adjacent to a faulted zone with marl horizons (section 2.2). The descriptions of the samples presented below correspond with the SEM images shown in Plates 3.12 to 3.20. The photomicrographs were taken in normal SEM mode unless otherwise stated.

3.3.1 TD 1 sample

Sample TD1 was obtained from a horizontal joint surface at the top of a prominent marl-rich bed close to the fault. In hand specimen the joint had an undulating surface, with abundant manganese spotting preferentially developed on local down dip breaks of slope (similar to Plate 2.7). No other mineralisation was apparent in hand specimen. Acicular calcite was not present on these horizontal surfaces, however the sample showed evidence of dissolution of the chalk matrix and local recementation. Many of the coccoliths exhibited signs of erosion by dissolution and individual plates or laths showed rounded edges, and calcite rhombs were present. Under relatively low magnification, in backscattered mode, the dendrites showed a radial dendritic pattern (Plate 3.12) composed of abundant individual manganese spots. Many such radial dendrites were associated with flattish grey patches (Plate 3.13) composed of clay (K, Al, Si rich) which appears to have acted as a substrate for precipitation of the manganese spot.

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3.3.2 TD 2 sample

Sample TD 2 was obtained from a vertical fracture surface adjacent to the fault. In hand specimen the manganese spots were strongly aligned in a dendritic pattern on the fracture surface (Plate 2.8). The dendrites appeared to splay out from the top of the fracture which was cross cut by a horizontal marl-rich joint (Plate 2.8) with abundant manganese spots. Under the SEM the fracture surface was relatively clean with well preserved coccoliths and foraminifera tests. One part of the surface, however showed extensive recrystallisation/erosion where the original structure of the chalk was destroyed, leaving a smooth pitted surface. Occasional ?detrital quartz grains were also noted.

3.3.3 TD 3 sample

Sample TD3 was collected from the joint surface of small fault north of the main fault. In hand specimen the fracture surface is grey-white, has a smooth texture, and exhibits abundant manganese spotting (Plate 2.6). At its thickest the manganese spots locally coalesce into a semi-continuous coating, sometimes showing a patchy parallel alignment to the local dip of the surface which in places had a slickensided surface (Plate 2.6). Under the SEM the fracture surface contained abundant wisps of clay (Plate 3.14), most probably illite (rich in K, Al, Si). Platy aggregates of recrystallised calcite were present on the surface of the fracture, although coccoliths were well preserved in other areas. The manganese spots had a similar geometry and botryoidal texture (Plate 3.14, lower left) to those described in TD 1 and TD 2, and spot analyses showed Ca, Si, Al, Co and Ni to be present as well as Mn.

3.3.4 TD 5 sample

Sample TD 5 was taken from the hanging wall of the fault. The fault aperture was locally enlarged with relatively smooth fracture surfaces, whereas in other parts of the fault zone it appeared to be intensely deformed and recrystallised along small shear zones. The enlarged apertures are inferred to have formed by dissolution and/or mechanical abrasion. The manganese spots did not show any evidence of deformation, but occasionally spots were aligned within slickenside grooves. Portions of the fault zone were heavily stained orange. Patches of euhedral quartz were present in small vuggy areas on the fault surface. Manganese oxide spots were abundant on the surfaces of the quartz crystals, but interestingly, no Fe-rich phases were present, although they were on the surface adjacent to the vugs.

The apparent slickensides were clearly visible under the SEM at relatively low magnification (Plate 3.15). Partially hollow circular structures were present on the surface and are interpreted as the surface expression of foraminifera or other shelly fragments which have undergone preferential dissolution. These generally appear to show no pervasive deformation indicating that recrystallisation has been the dominant control on the texture developed in these zones (linear structures on Plate 3.15). The manganese spots showed typical botryoidal textures draping the fracture surfaces (Plate 3.16).

3.3.5 TD 6 sample

Sample TD 6 was obtained approximately 10 m from the hanging wall of the fault, and was taken

from a bed of relatively soft white chalk which was heavily orange stained and contained pseudomorphed nodules of iron (hydr)oxide after pyrite. Some areas showed recrystallised textures similar to those found in TD 5 (Plate 3.15). Manganese spots were present as discrete spots, but were less abundant than near the fault zone.

Under the SEM the fracture surface was composed almost totally of secondary rhombohedral calcite varying individual crystals varying from < 1μm up to approximately 20 μm in diameter (Plate 3.17). No clays or acicular calcite were noted on the fracture surface. Botryoidal manganese spots were not found on the sample under SEM, however, backscattered imaging highlighted very small areas of high brightness contrast typical of manganese spots seen in other samples (e.g. Plate 3.18). At high magnification, these were found to be extremely unusual, small (3-5 μm) spheroidal structures, composed of abundant interlocking platelets, resting on the surface of the rhombohedral calcite. These are extremely similar to cristobalite "lepispheres" found elsewhere in the chalk (Schole, 1974) and in some respects to cockscomb barite or haematite. However, an SEM scan showed that these structures are composed of Mn, with lesser Ni and Ca and some Co, a composition similar to the larger botryoidal masses of manganese. Such manganiferous structures were not found in any of the other samples or previously reported in the literature. However, although cristobalite lepispheres are present in the chalk, such spherical structures are often assumed to be cristobalite. It is therefore possible that some have been mistakenly identified.

3.3.6 TD 9 and 10 samples

Samples TD 9 and TD 10 were collected from a marl band immediately adjacent to the footwall and hanging wall respectively. The fracture surface was a bedding plane fracture which displayed small undulations along the surface. Manganese spots were very abundant on the marl, and showed a distinct distribution: precipitation having occurred dominantly on the down dip areas of surface undulations. The most intense distribution occurred immediately below the break of slope and at the base of dip slopes, where amalgamation of individual spots was clearly seen Plate 2.3). Ferric rich clays were conspicuously absent from the surfaces of the marl bands.

Under the SEM, TD10 showed a scaly appearance with the development of platy cemented calcite (Plate 3.19) and some clay coatings. The surfaces were much finer grained than typical chalk and although calcite rhombs and coccolithic fragments were present, there was extensive recrystallisation (Plate 3.19). Acicular calcite was absent, but manganese spots were abundant. The manganese spots showed clusters with abrupt terminations associated with steeper down-dip slopes and hollows in the fracture surface. Qualitative analysis showed that Co, Ni, Al, Ca and Si were present in the manganese spots. Some of the manganese spots were associated with clays, which may explain the presence of Al and Si in the analysis.

3.3.7 TD 12 sample

Sample TD 12 was collected from an orange-brown stained area associated with pseudomorphed pyrite nodules. Under SEM the fracture surface was generally well preserved, but showed some recrystallisation and precipitation of calcite. Sparry calcite growth was present in foraminifera cavities. Manganese oxides occasionally showed an unusual spongy like texture forming on platy recrystallised calcite (Plate 3.20). Relatively abundant Si, Co and Ni were associated with the

manganese spots.

4. Results and discussion

The following section provides a synthesis of the results of the SEM study and briefly describes the depth trends in fracture mineralisation at Twyford Down. Although the SEM work is at an early stage, several preliminary conclusions are presented regarding the controls on precipitation processes and the spatial distribution of the Fe-rich clays, acicular calcite and manganese (hydr)oxides on the fracture surfaces of the chalk. The implications of surface mineralisation for pollutant transport will be discussed in Section 5.

4.1 Depth trends in fracture surface mineralisation

Three principal types of mineralisation have been described from the shallow unsaturated zone at Twyford Down. These are a) clay complexes including both secondary orange-brown Fe-rich clays and illite and probably smectite clays of unknown origin; b) fine grained white crusts composed of acicular calcite, and c) manganese (hydr)oxide spots. In addition, several fracture surfaces showed evidence of recrystallisation and secondary precipitation of calcite. There was a significant variation in fracture mineralisation in the vertical profile sampled, both with depth and at each sampling locality. Some of the fracture surfaces at 3.5 m, for example, showed extensive crusts of white calcite over Fe-rich clays, whereas others less than one metre away showed only Fe-rich clays or only manganese spots. Such spatial heterogeneity was also observed along the faulted section particularly with regard to Fe-rich clays and manganese (hydr)oxides.

Clay linings were present to varying degrees over the entire depth profile. The Fe-rich clays were best developed in the shallower parts of the section particularly at 1.2 m, but extensive mineralisation was present down to 3.5 m. Vertical and near vertical fault zones and major fractures generally showed extensive dark brown staining, but the local distribution within the fault zones was variable with some fracture surfaces showing intense colouration and others relatively little or none. There appears to be no preferential development of clay mineralisation on fracture surfaces with specific orientations, however Fe-rich clays were conspicuously absent from the horizontal bedding plane fractures of the marl bands. A strong development was evident on fractures associated with oxidation of pyrite nodules. Illite and probably other clays were much less abundant on most fractures and were most commonly found on major fractures and on the surfaces of the marl bands. The Fe-rich clays were always found to post-date manganese spots but were younger than the acicular calcite. The age of the illite and other clays is not known.

The calcite mineralisation was difficult to observe in the field unless particularly well developed, in which case it appeared as a smooth white precipitate. The acicular calcite mats showed a clear relationship with depth. Although present at 1.2 m, the calcites were relatively sparsely distributed and displayed a low aspect ratio. They also showed signs of partial recrystallisation and destruction (section 3.2.1). Their maximum development appeared to be between 3.0 and 3.5m where Fe-rich clays were often completely covered with a white crust of calcite. The areal distribution of the calcite crust was not as extensive as the Fe-rich clays and many fracture surfaces showed no evidence of these crusts. The higher density of acicular calcite at 3.0 - 3.5 m is accompanied by a large increase in aspect ratio (greater than 100). Below 3.5 m acicular

calcite needles were not found - John can you check your notes here.

Manganese spots were found at most localities visited at Twyford Down. The only exception was the very shallow part of the section (1.2 m depth) which was extensively coated with Fe-rich clay. Even after careful study and removal of the clays, no manganese spots were found. The density distribution of the manganese spots is highly erratic and an average value could not be ascertained. In general, manganese spots appeared to show irregular distributions even on single fracture surfaces. Their areal distribution was independent of that of Fe-rich clays, and where both occurred together the manganese spots were always present beneath the clays and therefore are assumed to be younger. It is interesting that qualitative analysis on the SEM showed Fe to be low or absent in the manganese spots. Manganese spots were, however, present as coatings on quartz crystals found in a small vug in one sample (TD 5). Manganese mineralisation was particularly well developed on samples collected from the larger faults and the marl bands. In sample TD5 the manganese spots were often aligned parallel to slickensides on the fault surface (Plate 2.6), but it could not be ascertained if these were deformed or recrystallised. The distribution of manganese spots in relation to undulations on the horizontal marl bands (Plate 2.7) and on vertical fractures (Plate 2.8) was unusual and is likely to be related to fracture flow.

Recrystallisation features were described for most of the samples taken from the structured chalk except the shallowest section due to the abundance of Fe-rich clays. Extensive recrystallisation was evident in the fault zone with linear striae observed under the SEM (Plate 3.15) and slickensides noted in-situ. The presence of rhombic calcite was, however, more typical of recrystallisation in the chalk away from the fault zones (Plate 3.17). The development of recrystallisation features on the surfaces of fractures in the structured chalk near large faults is consistent with field observations from Twyford Down for the development of relatively hard, re-cemented chalk matrix adjacent to some of the faults. The age and origin of this re-cementation are uncertain, however, the re-cementation probably developed in response to chemical potential gradients established between matrix and fracture waters and through initial matrix dissolution by unsaturated recharge waters. The surface of the marl bands was unusual in that recrystallisation has led to the development of a scaly surface with patches of platy micritic calcite. It is not clear whether this is related to the abundance of clays or to uptake of strain along marl horizons during deformation. The study of both fracture mineralisation and recrystallisation features is therefore a potentially powerful tool in the investigation of both the flow mechanisms and geochemical processes in the chalk aquifer.

4.2 Manganese oxides

Manganese spots most commonly occur as isolated star shaped aggregates and as branching dendrites on vertical fracture surfaces. The SEM studies have shown that these are much thinner than previously reported precipitates in freshwater stream and lake environments (e.g. 7-57 µm: Robinson, 1993; several mm: Buckley, 1989). The manganese spots studied were always the oldest precipitates of those studied, and no unequivocal instance was found where the spots were present on the Fe-rich phase or the acicular calcite phase. They were, however, present on secondary euhedral quartz crystals of probable diagenetic origin developed in vugs in one sample.

The manganese spots generally show no preferred alignment, simply forming individual star

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shaped aggregates. Transient flows may have occurred across these fractures surfaces, but the partially wetted fracture surface may have provided adequate physical and chemical conditions for the precipitation of these minerals without flow through the fracture. However, the development of strongly aligned spots and the development of local variations in spot density as a function of microtopography suggests that these spots developed while flow was occurring through the fracture.

One striking aspect of the distribution of the manganese spots is that they generally appear to be independent of the distribution of the Fe-rich clays, and where both occur it is clear that the manganese spots are older and discrete from the ferruginous coatings. Most manganese spots are found as isolated black spots on white chalk surfaces with little or no ferruginous coatings. These manganese spots are also very low in Fe compared to other manganiferous precipitates. Giovanoli (19**) whilst studying manganese dendrites from the Solnhofen chalk deposits, also noted that Fe and Mn showed different behaviour and were locally separated.

Manganese is present at levels of 100 - 200 mg/kg in the chalk, most likely present as Mn^{2+} in solid solution in the low-Mg calcite, and is thought to be liberated during dissolution of the chalk matrix (Edmunds et al., 1987). The very low values of Mn the oxidising zone shows that the Mn is removed from solution relatively quickly.

Primary controls on the precipitation of manganese oxide phases in freshwater systems are the subject of much debate, specifically the roles of physicochemical vs. biological processes (Nowlan et al., 1983; Robinson, 1993). There is abundant evidence that manganese (and iron) oxidising bacteria are closely associated both with freshwater and marine manganese oxides (Ehrlich, 1966; Mustoe, 1981). Spherical structures resembling those found in sample TD6 (Plate 3.18) and the spongy textures in TD 12 (Plate 3.20), have generally only been produced by bacterial precipitation (Mustoe, 1981; Hariya & Kikuchi, 1964), suggesting that Mn-oxidising bacteria may have played a major role in the genesis of the manganese dendrites in the chalk. Such an interpretation is also supported by experimental studies which indicate the difficulties of precipitating manganese (hydr)oxides. Diem and Stumm (1983) showed that sterilised lake waters undersaturated with $MnCO_3$ or $Mn(OH)_2$, in the absence of catalysts, remained unoxidised for periods in excess of seven years in the presence of dissolved oxygen. Most of the manganese was lost from solution after six years in the presence of buserite, and measurable oxidation rates were found in solutions oversaturated with $MnCO_3$. However, when manganese-oxidising bacteria collected from the lake were added rapid oxidation of manganese occurred and most of the manganese was precipitated in only eight days (Diem & Stumm, 1983).

Previous studies, where spherical structures have been found, have generally interpreted these to be related to bacterial activity (Greenslate, 1974; Robinson, 1993). In general, manganese is precipitated as extra cellular deposits (Mustoe, 1981). The production of minerals by microorganisms takes place through adsorption, which decreases the activation energy required for spontaneous nucleation, or through metabolic activity, which leads to changes in solution chemistry and oversaturation of a mineral. The precipitates formed through the activity of microorganisms are often in a poorly ordered, near amorphous state related to high rates of nucleation and precipitation (Ferris, 1995). Such precipitates have high surface reactivities and, therefore, the ability to adsorb dissolved inorganic and possibly organic solutes.
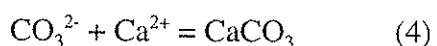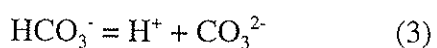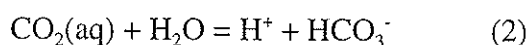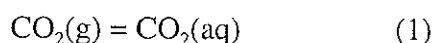
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The location of bacteria in aquifers is governed by the transport of bacteria to the solid surface, initial adhesion, anchoring of cells with special cell structures and formation of biofilms (Bosma & Zehnder, 1994). Bacterial precipitation, as with physico-chemical processes may be indicators of flow through fracture systems. Although bacteria have been found in both the unsaturated and saturated zones of the chalk down to depths of greater than 40 m (Towler et al., 1985; Clark et al., 1991), there is little information on the role of manganese oxidising bacteria.

As well as the biological processes, physico-chemical processes may also be important since Mn (and Fe) solubility is strongly redox dependant. If physicochemical were the dominant control in the precipitation of Mn spots then their presence would generally be located close to strong Eh/pH gradients. It is unlikely that strong Eh gradients exist in the shallow chalk aquifer at Twyford Down, but differences in pH may occur between the matrix pores and fracture waters, which could lead to precipitation of manganese (oxy)hydroxides following dissolution of the chalk in the soil zone or along fracture surfaces. Since homogeneous nucleation is a kinetically slow process, precipitation and growth will most likely occur on existing manganese spots.

The roles of physicochemical and biological controls on the distribution of the manganese spots requires a detailed microbiological study, particularly to ascertain the presence of Mn oxidising bacteria in the aquifer. The presence of manganese spots are confined to fracture surfaces in the chalk and this may simply be due to the relative sizes of bacteria and the small pore throat diameters in the chalk matrix which makes it likely that bacterial processes are likely to be restricted to fracture surfaces or the pores immediately adjacent to fractures. In addition, the unusual distribution of the manganese spots in hollows and on the leeward sides of undulations on the marl bands may simply be due to protective sites for bacteria against rapid flow. It is evident that some features of the manganese spot distribution is related to fracture flow and the presence of hydraulically active flowpaths. These include the extensive precipitates on marl bands and major faults and the splays on vertical fracture surfaces, as well as their confinement to open fractures as discussed above. The distribution of manganese spots may, therefore, be useful indicators of fracture flow in the shallow chalk.

4.3 Calcite precipitation and recrystallisation

The solute major element chemistry in the shallow chalk aquifer is largely controlled by reactions involving CO_2 and gives rise to water which rapidly attains saturated with calcite. Reactions in the CO_2-H_2O system are governed by the following equilibria:

$$CO_2(g) = CO_2(aq) \qquad (1)$$

$$CO_2(aq) + H_2O = H^+ + HCO_3^- \qquad (2)$$

$$HCO_3^- = H^+ + CO_3^{2-} \qquad (3)$$

$$CO_3^{2-} + Ca^{2+} = CaCO_3 \qquad (4)$$

Carbonic acid is produced in the soil zone and soil pCO_2 can be significantly higher than that of the atmosphere. The amount of dissolution of calcite is controlled primarily by pCO_2 and the

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high soil values will cause significant dissolution of chalk according to the reaction:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3 \qquad (5)$$

The rate of dissolution of carbonates is surface controlled being determined by reaction at the water-mineral surface. In chalk this takes place extremely rapidly owing to the very fine grain size and hence large surface area of the matrix chalk. Calcite saturation in the chalk is reached at very shallow depths, generally within one metre of the surface and thereafter bulk dissolution is inhibited (Edmunds et al., 1992). Reprecipitation of calcite is attained either through movement of the solution to areas of lower pCO_2 or to evaporation which leads to saturation or supersaturation. Reprecipitation of calcite is well known in alkaline soils developed on carbonate rocks (Salomons & Mook, 1976). The presence of aragonite in meteoric vadose zones is also well established (Curl, 1962), often in settings which have undergone rapid evaporation or CO_2 degassing (Given & Wilkinson, 1985). The dissolution and precipitation of carbonate, although a simple reaction, is complicated due to trace element inhibitors, open or closed system behaviour with respect to CO_2, kinetic controls, ion pairing and mixing. High concentrations of organic ligands may enhance dissolution rates of calcite, but dilute concentrations of organic ligands (< 100 µM) may in fact decrease dissolution rates due to complexing and adsorption of the ligands onto surface dissolution sites such as kinks or steps in the lattice structure (DeMaio & Grandstaff, 1995).

The most important controls on the degree of calcite solubility and saturation are the soil PCO_2 which is temperature dependant, the kinetics of calcite dissolution and the flux of CO_2 between the soil and groundwater through the unsaturated zone (Pitman, 1979). In the summer, soil moisture volume in the chalk is low and is expected to be saturated with respect to calcite because of high pCO_2 and long residence time. In contrast, during the winter periods where residence times are low (Pitman, 1978) soil waters are generally undersaturated. It is likely that open system conditions exist throughout the profile at Twyford Down because the aquifer is unconfined with a large depth to the water table. Edmunds et al. (1992) noted that the greatest variation in volumetric moisture fraction of the unsaturated zone of the chalk was located in the uppermost part of profiles (ca. 2.5 m), which defined the maximum depth (the zero flux plane) where the upward movement of water can take place. Seasonal and daily fluctuations may have a significant effect on solute chemistry in this shallow part of the aquifer, particularly where evapotranspiration is high.

The acicular calcite crystals and felted mats developed in the vertical profile at Twyford Down are similar to those described as "needle-fibres" (Phillips & Self, 1987), or "whisker crystals" (Calvet, 1982) and are well documented in recent calcrete-caliche and spelean deposits (Strong et al., 1993). Any hypothesis for the precipitation of these calcite mats in the chalk has to take into account the following observations:

1) the needle-like habit of the calcite needles
2) shallow distribution and maximum development at 3.0 - 3.5 m.
3) development of large (up to 500 µm diameter) pores with tangentially arranged needle calcite.
4) presence of occasional undecomposed rootlets preserved "within" calcite mats.

The alteration and precipitation of carbonates is important in the formation of calcrete crusts and

acicular calcite is a common in the development of such sub-aerial formations. Acicular calcites have been found to from felts or crusts where crystals are numerous in calcareous crusts (e.g. James, 1972). The shape of precipitated calcite crystals is dependant on several factors such as rate of crystallisation, degree of oversaturation and the presence of other solute constituents e.g. high SO_4 and Mg (James, 1972; Given & Wilkinson, 1984). During slow crystallisation, large euhedral crystals would be expected to grow, whereas rapid crystallisation will lead to dendritic, acicular crystals commonly found in quenched systems. At low supersaturation, calcite would be expected to show normal growth and crystal shapes, but at high degrees of supersaturation they exhibit acicular, dendritic or whisker shapes (James, 1972). Acicular crystals present in the vadose pores are only known where precipitation is driven by rapid degassing of CO_2 and/or evaporation which have led to supersaturation (Given & Wilkinson, 1984). During rapid CO_2 degassing carbonate ions are rapidly formed through dissociation of HCO_3. The small size and acicular nature of the calcite crusts at Twyford Down, therefore, suggest rapid crystallisation from supersaturated solutions.

Rapid organic matter mineralisation in soils is also known to lead to supersaturation of calcite in soil solutions. This is due to the persistence of high HCO_3 and Ca due to the slow precipitation kinetics of calcite (Amrhein et al., 1993) and the inhibitory effect of organic matter blocking crystal growth sites (Inskeep & Bloom, 1986; Amrhein & Suarez, 1987). In the present study the maximum development of calcite was present well below the soil and shallow root zone (the soils themselves were not studied) and only a few thin plant roots were noted. Soil water with high PCO_2 developed in the root zone during biotic growth would be expected to degas as the water moves into the chalk zone of lower PCO_2 (closer to atmospheric) and may explain the confinement of calcite to less than 3.5 m depth.

It is considered that the calcite needles were formed by rapid precipitation from highly supersaturated solutions in agreement with James (1972), and that supersaturation was induced by either rapid degassing of CO_2 and/or evapotranspiration through development of the zero-flux plane during summer months. High PCO_2 occurs in soils during the warm summer months when biotic growth is at a maximum and it is during this period that evapotranspiration is at a maximum. It is difficult, therefore, to separate these processes and it is likely that both have been important. The maximum depth of calcite precipitation correlates with the approximate depth expected of the zero-flux plane in the chalk. It is possible that a more general control on the occurrence of the calcite mats is due precipitation from supersaturated zones around roots and the root zone. The common occurrence of such textures around root voids (Harrison, 1977; Calvet and Julia, 1983; Strong et al., 1992) forming alveolar structures is consistent with an hypothesis where supersaturation is controlled by evapotranspiration. The maximum development of calcite in the present study, however, is well below the root zone. There is also a lack of development of calcite froming tubiform structures (Strong et al., 1992) which may indicate such a process. Although roots were noted in the calcite mat, these were not particularly common and thought to have originated by being washed down from the root zone. The development of a zero flux plane may still allow supersaturation at shallow depth as water moves upward to satisfy evapotranspiration demand.

Several recent studies have suggested that biotic processes are responsible for the production of needle-calcites. The similarity of the size and arrangement of acicular calcite to fungal hyphae has been taken as evidence that calcite precipitation is related to fungi or bacteria (Wright, 1984;

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Phillips & self, 1987). Wright (1986) considered that fungi, which both accumulate and transport nutrients to root cells, are responsible for needle-calcite through calcification of fungal hyphae. Phillips & Self (1987) found two distinct sizes of calcite needle-fibres which they interpreted as having different origins: short "micro-rods" were probably calcified rod-shaped bacteria and larger needle-fibres were formed within mycelial strands. A direct origin for the organic development is however very difficult to establish, in particular because the areas where organic activity is high are generally those where rapid fluctuations in water content and evapotranspiration are greatest i.e. in the shallow soil and vadose zones. Evaporation was discounted by Strong et al. (1992) in a study of recent micrite and needle-calcite in an esker in Yorkshire on the basis of a lack of fractionation of stable isotopes which would be expected. However, the present hypothesis with saturation reached by evapotranspiration or rapid CO_2 degassing is consistent with the data since evapotranspiration does not fractionate stable isotopes. The acicular calcite from Yorkshire also had $\delta^{13}C$ values of approximately -10 to -11, intermediate between soil derived CO_2 and derived carbonate consistent with reaction (5). There is no direct evidence (or necessity) for precipitation of calcite due to micro-organisms in this study (Wright, 1983, 1986), however, such an hypothesis cannot be discounted.

It has been noted previously that needle-fibre calcite easily disintegrate or recrystallise to micrite (Knox, 1977; Calvet and Julia, 1983; Wright, 1984, 1986) and calcite needles are commonly associated with abundant micrite (Wright, 1984; Strong, 1992). Due to the delicate nature of these calcite needles and the fact that they easily recrystallise to micritic calcite, their long term preservation is highly unlikely unless they have been protected from any form of water flow. This is considered to be extremely unlikely in the present study because the presence of manganese and iron oxides (as well as the calcite itself) indicates that the fractures are hydraulically active. It is postulated, therefore, that the calcite needles are very recent (perhaps less than one year from the development of the most recent ZFP). A young age is also indicated by the fact that roots are still preserved within the felted mat of some samples. There is some evidence of recrystallisation in the shallowest zone (1.2 m) of the profile where micritisation has occurred and diffuse edges to some crystals were present (Plate 2.3).

It is considered likely that winter recharge waters, unsaturated with respect to calcite, would destroy the delicate needle-calcite. Such flow is thought to have caused recrystallisation of the carbonate on fracture surfaces, as indicated in Plate 3.3 at the sample collected from 1.2 metres. Recrystallisation is also responsible for rhombohedral calcite such as shown in Plate 3.17, but there is no evidence for assuming that recrystallisation of acicular calcite has occurred here. Samples from the soil zone may highlight some of the processes already discussed and would provide valuable information on precipitation/recrystallisation processes. As noted by Strong et al. (1992) acicular needle fibre textures are not confined to arid regions of the world, but may be formed during dry periods in temperate or cold climates. Their general occurrence in arid and semi-arid environments is simply related to the greater chance of preservation.

4.4 Fe-rich phase and clays

The majority of clays in near surface environments are formed through recrystallisation or incongruent dissolution of silicate and it is rare to find clays resulting from aqueous precipitation (Velde, 1992) eg. sepiolite from seawater. It is thought that nucleation occurs in the presence of

another phase (Nagy, 1995) but in topotactic nucleation (Banfield & Barker, 1994),where the dissolving mineral loses cations but forms building block for crystallisation, the solutions may be undersaturated with the precipitating phase (Casey et al., 1993). The chemical reactions involved in clay genesis are thus often complex and difficult to establish.

Significant amounts of clay and terrigenous material are present in the Lower Chalk, dominantly smectite and quartz (Bath & Edmunds, 1981). Montmorillonite occurs as the dominant clay in most formations and is particularly abundant in the Upper and Middle Chalk (Morgan-Jones, 1977). The origin of the montmorillonite has been the subject of debate with both neoformational origin and volcanic origin being suggested. Kaolinite is less abundant and often considered to detrital in origin (Morgan-Jones, 1977) but may in part be derived from alteration of glauconite. The presence of muscovite and illite is also considered to be detrital origin. Clays are most abundant in the marl bands and in some of the major faults at Twyford Down but they are not particularly abundant on most fracture surfaces. They are, however, important as a major control on the cation exchange properties of the chalk, and may also be an important local control on the distribution on manganese spots (Plates 3.12 and 3.13).

The most conspicuous clay fracture mineral at the Twyford Down site was the orange to dark brown phase assumed initially to be ferric (oxy)hydroxide. These were found to form extensive amorphous looking drapes over much of the fracture surfaces under SEM. Qualitative analysis, however, showed that these drapes were also rich in Al with K, Si and Ca detected. It was not determined whether these phases were amorphous in nature or whether they represented crystalline Fe-rich clays (eg. nontronite) or a mixture of clays and Fe (oxy)hydroxides and further work (XRD) is necessary to establish the identity of the phase. These clays are most evident in the upper parts of the profile and in beds associated with oxidised nodular pyrite. It is thus likely that the ultimate source of the Fe is from the oxidation of pyrite. The origin of the Al and K is most likely to be derived from clays but the actual formation and controls on formation are not yet established. The role of biochemical reactions in redox processes in Fe-rich systems is well known but its role in production of the Fe-rich clays is not known. Geptner et al. (1995), in a study of Fe-rich clays in Iceland have found that biochemical processes play an important role in the formation of a Fe, Al, K, Si rich gel which acts as a precursor of the clay minerals. The surface reactivity of these fracture minerals is likely to be extremely high and likely to from an effective retardant to the transport of many solutes in the shallow unsaturated zone.

It is suggested that the source of the Al is colloidal clay originating from the soil horizons. The solubility of Al is extremely low at the high pH values typical of chalk. These are likely to have been periodically washed down through the fracture system at times of high recharge and deposited on the wetted walls of the fracture. It is feasible that adsorption of colloidal clays onto an original ferric (oxy)hydroxide surface may lead to formation of Fe-rich clays.

5. Implications for contaminant transport

At a regional scale, fractures are an important control on the geomorphology of the chalk and on weathering processes, as well as controlling transport at both the regional and local scales. Dissolution and/or precipitation reactions can cause significant changes in the buffering and sorbing capacity of fracture surfaces. Therefore, an understanding of the geochemical processes occurring at the matrix-fracture boundary, where reaction-induced porosity increase or decrease may take place, as well as secondary mineral formation, is fundamental to modelling the physical and chemical retardation of contaminants through an aquifer.

Even where matrix tension is high and flow would not be expected in fractures, the presence of mineralised coatings, particularly clays, may effectively form a barrier with respect to water movement and solute diffusion across fractures. Where mineral coatings do not significantly affect water movement, surface processes may still exert a strong selective influence on solutes. A knowledge, therefore, of the type and extent of mineralisation of secondary phases on fracture surfaces is essential to understand the transport behaviour of natural and anthropogenic solutes through the unsaturated zone. The presence of fracture mineralisation affects the chalk aquifer in two ways: firstly it will affect the retardation of selective solutes and contaminants, and secondly it will affect diffusion between the fracture waters and pore waters of the chalk. In addition, it is likely that the transfer of water itself between fractures and pores will be significantly affected and may lead to enhanced fracture flow even when matrix suction is theoretically high. It is feasible, and even likely, that fracture flow will occur through the unsaturated zone along fracture surfaces in cases where current theoretical models indicate that flow should not occur. By-pass flow has indeed been postulated as a mechanism from a study of tritium and nitrate profiles in the chalk (Geake & Foster, 1989). The distribution of surface mineralisation is likely to complicate theoretical calculations of flow but this study shows that the distribution of secondary minerals is likely to be heterogeneous on a local as well as regional scale.

The ability of the shallow chalk aquifer to act as a chemical barrier to the transport of metals and other pollutants through the unsaturated zone is largely due to the excellent buffering capacity of the chalk to neutralise acidic solutions and the limited solubility of many heavy metals at high pH. This is evident for the distribution of Mn, Fe and the Fe-clays on fracture surfaces, which themselves inhibit the transport of other solutes by adsorption processes. These phases will exert a strong influence on the chemical composition of recharge waters as well as contaminant transport and matrix-fracture interaction.

The presence of clays and (hydr)oxides are likely to impose significant changes on the natural solute geochemistry as these are important cation exchange sites. They can also be of great importance in the retardation of cationic and some neutral species introduced to the aquifer as a consequence of surface and underground waste disposal or accidental spillage of pollutants. The rate of advance of a pollution front can be modelled by the equation:

$$v_a^+ = \frac{v}{1 + (\rho/\phi)K_d}$$

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where v_A^+ is the velocity of the A^+ concentration profile, v is the velocity of water, ρ is the bulk density of the sediment, ϕ is the porosity of the sediment and K_d is the distribution coefficient (Drever, 1988). The expression $1 + (\rho/\phi) K_d$ is the retardation factor. Values of ρ/ϕ are typically 5 to 20 for aquifers and, therefore, unless K_d is very small, retardation will have a large effect on solute transport. The K_d values of amorphous phases is likely to be extremely high and these phases on the chalk fracture surfaces are, therefore, extremely important. Removal of the shallow chalk may therefore have significant effects on the short term transport of pollutants. Of course, there are many chemical species which are not appreciably adsorbed, and although adsorption may remove some chemicals efficiently form pollutant sources, it is subsequently difficult to remove these should aquifer remediation be required. Should the local environment change significantly eg. due to changes in depth of the water table or to chemical changes imposed by a pollution incident, the fracture surface mineralisation will change towards a new equilibrium or steady state assemblage. Inputs of eg. highly reducing agricultural waste may locally cause dissolution of (oxy)hydroxide phases and remobilisation of sorbed species.

Although manganese (hydr)oxides are very abundant on fracture surfaces their overall surface coverage on fractures is relatively small. It is thought that their effects on major changes in porosity and permeability will be much less than the more extensive Fe-rich phases. It is, however, well established that these oxides have the ability to co-precipitate and scavenge a wide range of metals and are, therefore, important in adsorbing and retarding metals through the aquifer. Many of the fracture phases studied appear to be amorphous in character which would imply extremely high surface reactivities. The fact that secondary mineralisation occurs on most fracture surfaces indicates that flow is important along all of these surfaces. Normal faults are present and may act in a similar manner to the small-scale, closely spaced, normal faults noted by Brewster et al. (1986) in the North Sea which provide pathways for large-scale fluid movement. The concentration of manganese precipitates and dissolution features along the faulted section would indicate that this section has been important as a conduit for extensive fluid movement. Iron-rich clays were also abundant on the major faults at Twyford Down implying that these are important conduits for the transfer of water and solutes through the unsaturated zone.

The occurrence of relatively impermeable marl bands is expected to have very significant effects on the flow of water through both the unsaturated and saturated zones. The extremely abundant manganese spots and their distribution on the marl bands at Twyford Down is evidence that these are important for the lateral transfer of water in the unsaturated zone. It is likely that the chalk above such zones may be saturated for much of the time forming local perched water tables. Indeed, high discharges of water by lateral flow along marl bands along coastal cliffs of the chalk in France have been noted (H. Jones, *pers. comm.*). The abundance of marl bands may, therefore, provide rapid pathways for pollutant transport laterally through the chalk even where retardation through coupled advection/diffusion is an important control throughout the aquifer as a whole. Retardation may nevertheless be important for selected solutes on marl bands due to adsorption onto manganese (hydr)oxides and clay mineral surfaces.

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6. Summary and Scope for further work

The results of the present study are important because they represent the first detailed investigation of the micromorphology of (oxy)hydroxide, clay and carbonate precipitates on chalk fractures and can be used to provide information both on the origin of the precipitates, and their likely effects on porosity and permeability of the fracture surfaces. Although a limited number of fracture surfaces have been studied, a wide range of fracture minerals have been found.

Iron-rich clays originally thought to be ferric (hydr)oxides are considered to be Fe-rich clays. It is postulated that Fe is derived from the oxidation of pyrite/marcasite nodules and possibly from the soil, with (?)colloidal clay particles being adsorbed onto fracture surfaces with ferric-hydroxide. It is suggested that these eventually form amorphous looking clays with high surface reactivity. Manganese spots (star shaped aggregates) are likely to have formed through bacterial mediation on fractures surfaces. Early spongy or lepisphere-like structures are thought to form initially, before further precipitation into botryoidal amorphous precipitates. Needle-calcite crystals developed in one section are thought to form during summer months from solutions super-saturated with calcite. Their crystal structure and distribution is considered to be due to the rapid development of a zero-flux plane and/or CO_2 degassing of soil derived solutions. The extremely delicate nature of these and the presence of small undecomposed rootlets is taken as evidence for a recent origin for the calcite. The oldest fracture mineral phases are the manganese spots followed by Fe-rich clays with the acicular calcite being the youngest.

All of the phases studied require hydraulically active surfaces in their formation and their distribution on fracture zones is therefore considered to provide important information on flow pathways through the unsaturated zone of the Chalk aquifer. This is highlighted for the marl horizons which have abundant manganese mineralisation and are considered to be major conduits for flow. The fracture minerals are important in the retardation of solutes and potential contaminants through the aquifer, but their distribution, both locally and regionally is poorly known.

There is considerable scope for further work on fracture surfaces and fracture mineralisation and some of the problems and questions posed by this preliminary study are highlighted below:

1) The regional distribution, type and quantity of mineralisation on chalk fracture surfaces is not known. This is also the case for the distribution of fracture mineralisation with depth. Most petrological studies of the chalk have ignored secondary mineralisation but monitoring and characterisation of these should be seen as part of standard petrological description.

2) The structures of the minerals, which are fundamental to an understanding of their adsorption/retardation capacities is not known. An XRD and chemical study of individual (hydr)oxide phases is essential to identification of the phases and of their degree of crystallinity. A stable isotope ($\delta^{18}O$ and $\delta^{13}C$) study of the acicular calcite phase would be likely to shed light on their origin with regard to inorganic/organic control and the origin of the C (soil/rock derived).

3) The origin of the various components and physico-chemical conditions of formation of the

fracture minerals is not understood in detail. Further geochemical and SEM studies of chalk mineralisation is required, particularly on chalk from other areas and from borehole samples. A detailed study of bacteria associated with the various fracture minerals is strongly recommended in conjunction with geochemical studies to ascertain the role of biochemical processes.

4) The effects of fracture minerals on the diffusion of solutes and water across fracture surfaces is essential to the modelling of fluid flow in the chalk. Experimental laboratory studies are considered to be extremely difficult, but theoretical modelling combined with observational and field studies may lead to a more realistic approach to the problems of flow in the unsaturated zone of the chalk.

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