Chapter Number

Hydrogeological Significance of Secondary Terrestrial Carbonate Deposition in Karst Environments

V.J. Banks[1,2] and P.F. Jones[2]

[1]*British Geological Survey, Kingsley Dunham Centre, Nicker Hill, Keyworth, Nottingham*
[2]*University of Derby, Kedleston Road, Derby*
UK

1. Introduction

A significant hydrogeological characteristic of karst environments is the precipitation of a proportion of the dissolved calcium carbonate derived from limestone dissolution. The study of such secondary deposits is important because they provide information on the palaeohydrogeology of the unsaturated zone at the time of precipitation. They also offer the potential to provide information with respect to climatic conditions through the study of stable isotopes and dating through the study of radiogenic isotopes. This chapter introduces the formational processes, depositional environments (hydrogeological, hydrogeochemical, biological and geomorphological) and post depositional history of secondary terrestrial carbonate deposits. Consideration is given to the associated research themes and techniques, in particular to the current research focus on the role of microbial communities in present day sediment-water interface processes (Pedley and Rogerson, 2010) and the implications for furthering the understanding of climate change and landscape evolution. These deposits have a world-wide distribution (Ford and Pedley, 1996; Viles and Goudie, 1990) and include speleothems, travertines, tufas, calcareous nodules, calcretes and carbonate cements, such that speleothems and tufa represent two end members of a continuum of freshwater carbonate (Pedley and Rogerson, 2010). They form in a range of climatic conditions, but are best developed in warm humid climates. Examples cited in the text include case studies from the White Peak, Derbyshire UK, which currently experiences a temperate humid climate and hosts a range of deposits as a consequence of its recent geological history. The White Peak was not subjected to glacial erosion during the most recent (Devensian, MIS 2-4) glaciation, therefore there is a potential for an extensive record of Quaternary palaeoclimatic conditions to be preserved in the secondary carbonate deposits.

2. Types of secondary carbonate deposit and their classification

Secondary terrestrial carbonate deposits include four major groups: *(i) Speleothems* that are characteristically deposited in caves above the water table (vadose or unsaturated zone) from saturated mineral solutions and can be seen at scales that range from millimetres to tens of metres. Typically, they are formed of calcium carbonate by the precipitation of calcite

1   or aragonite from water as excess dissolved carbon dioxide is diffused into the cave
2   atmosphere. Aragonite is a metastable polymorph of calcite, which predominantly occurs as
3   acicular crystals in speleothems. Its occurrence is generally attributed to depletion of
4   calcium ions in magnesium rich solutions. Other minerals, for example gypsum, can also be
5   precipitated in this environment. They occur as *dripstones,* formed by water dripping from
6   the ceilings or walls of caves (*stalagmites* or *stalactites*), or as *flowstones* formed on the walls or
7   floors of caves. Speleothems can also form carbonate cements and cemented rudites in the
8   cave environment. Typically they form as elongate (columnar) crystals perpendicular to the
9   growth surface (palisade calcite, Kendall and Broughton, 1978), which may be visible as a
10   series of growth layers. Speleothems commonly comprise alternations of soft and hard
11   calcite (Ford and Williams, 2007) with most hard calcite occurring as palisade calcite, or as
12   microcrystalline calcite. They also occur outside the cave environment, e.g. the anthropogenic
13   flowstone precipitating from lime-rich cement at Lindisfarne Castle, Northumberland, UK
14   (Figures 1 and 2). (ii)*Tufa* (ambient temperature, freshwater carbonate with carbon dioxide
15   derived from the soil atmosphere) *and travertine* (carbonate precipitating from water that is hot
16   as a consequence of deep circulation with carbon dioxide being derived from magmas and
17   decarbonisation). These carbonates result from a combination of biologically moderated
18   physicochemical processes and accumulate in a range of settings. They may take the form of
19   cones, cements, barrages at metre to kilometre scale or minor, localised plant encrustations.
20   Growth increments in tufas occur as contrasting laminae of dense micrite and more porous
21   sparry crystalline calcite (Andrews and Brasier, 2005). (iii) *Carbonate cements* comprise minerals
22   that fill pore spaces and bind particles together. Most terrigenous clastic sediments (rudites,
23   arenites and argillites) have the potential to become cemented by minerals that fill the pore
24   spaces. Although beyond the remit of this chapter, common cementing materials also include
25   silica, iron oxide and sulphates. Carbonate cements occur externally to and within cave
26   environments. Within caves they typically occur as cave breccias (deposits of calcium
27   carbonate formed where cave water percolates into clastic sediments) and externally they
28   typically comprise a greater variety of cemented rudites (e.g. fluvial gravels or screes; Figure
29   3). (iv) *Pedogenic carbonates* encompass caliche, soil nodules and rhizome (root) coatings, which
30   may also exhibit incremental growth patterns. Fossilised forms include algal burrs, such as
31   those of upper Jurassic age in Dorset, UK (Francis, 1984). These carbonates can be either
32   inorganic or as consequence of biomineralization. Subsequent dissolution can lead to the
33   development of third-order forms.

34   Secondary carbonate deposits attract a plethora of terminology (Ford and Pedley, 1996;
35   Pentecost, 1995; Pentecost and Viles, 1994; Viles and Goudie, 1990, and Viles and Pentecost,
36   2007). Field descriptions are largely derived from the terms that are applied to microbialites
37   (biolithite of Folk, or boundstone of Dunham [Tucker, 2011]), encompassing stromatolites
38   and bioherms (Tucker, 2011; Viles and Goudie, 1990; see glossary). They may adopt
39   columnar, planar, or oncolite forms. According to Pedley (1990) tufas can be described as
40   either autochthonous (forming in-situ), e.g. phytoherm framestone (anchored) and
41   phytoherm boundstone (dominated by the heads of skeletal stromatolites), or clastic (not
42   anchored). Clastic tufas include: phytoclasts, oncoids, detritus, peloids and palaeosols.
43   Petrological descriptions of cements are usually based on the extent of micrite (carbonate
44   particles <4μm diameter) or sparite (clear, or white coarser equant calcite precipitated in

1 pore space between grains; Tucker and Wright, 1990). Reference should be made to the
2 literature for more unusual cement forms.

3
4 Fig. 1. Speleothem (flowstone) attributed to carbonate leaching from lime rich mortar,
5 Lindisfarne Castle, Northumberland, UK.
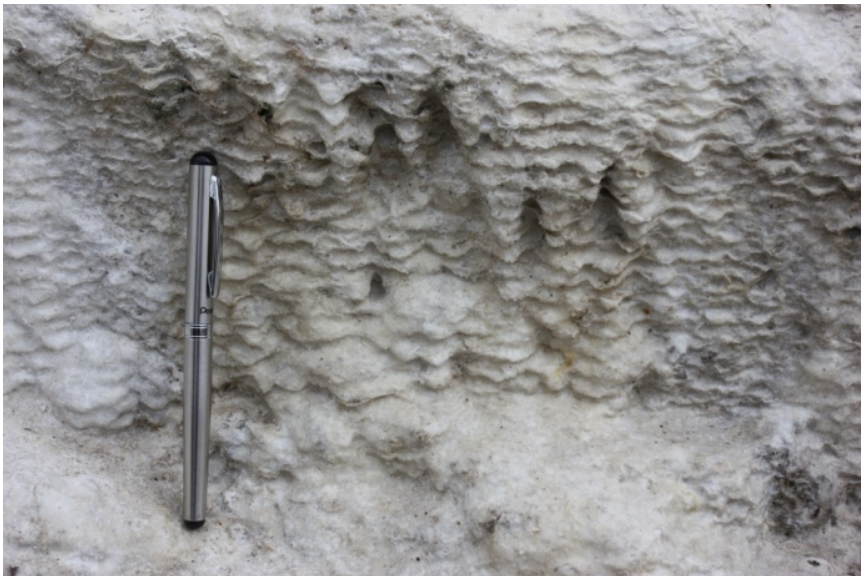
6
7 Fig. 2. Speleothem (flowstone) attributed to carbonate leaching from lime rich mortar,
8 Lindisfarne Castle, Northumberland, UK.

Fig. 3. Cemented scree at Ecton, Manifold Valley, Staffordshire, U.K.

Classification and interpretation of depositional environments is fundamental to the applied geological aspects of secondary carbonate deposits. Owing to the breadth of depositional environments and their global distribution, a number of potentially useful classification schemes have been developed. Classifications that have been applied to the major groups follow.

2.1 Speleothems

Speleothems are generally classified according to their morphology or their origin (Hill and Forti, 1995). The former is used more frequently and Hill and Forti (1995) use the term *speleothem type morphology* to define a distinct morphology that is controlled by one or more hydrological mechanisms, e.g. dripping, flowing, pool, geyser, capillary, condensation and aerosol water. More broadly, speleothems can be classified as gravitational (dripstones and flowstones), which are the key focus for this chapter, or as non-gravitational erratic forms, including coverings or shields, helictites (capillary-fed), botryoidal forms, moonmilk, pendants, straws, cave pearls, rimstones and pool deposits. Each of these is associated with a specific setting within the cave environment (Ford and Williams, 2007; Hill and Forti, 1995). Whilst stalactites and stalagmites are formed by dripping water, flowstone is formed layer upon layer by water flowing over surfaces. Draperies (e.g. curtains) may be formed by both processes separately or in combination. As a consequence of their layered structure, gravitational speleothems can be dated and contribute evidence of local and regional tectonic histories. They can also be used in conjunction with stable isotope analyses for the interpretation of climate change (section 6). Where flowstones occur, indicators of historic flooding may be preserved on cave walls as erosional features or inclusions of detritus.

2.2 Travertine and tufa deposits

The basis for the classification of the depositional environments associated with travertines and tufas comes from the work of Chafetz and Folk (1984) who defined five main classes: waterfalls; lake-fill; sloping mound or fan; terraced mound and fissure ridge. A number of classification systems have followed, which are broadly based on depositional setting, geomorphology or biology (Pazdur et al., 1988; Pedley, 1990; Pentecost and Lord, 1988; Pentecost and Viles, 1994; Viles and Pentecost, 2007). Additionally, classifications have been devised for engineering purposes; such classifications need to take account of the heterogeneous nature of tufa, e.g. the engineering classification of tufa in the Antalya area, SW Turkey (Dipova, 2011), which was derived from a consideration of primary fabric, diagenesis and strength. Pedley (1990) subdivided tufas on the basis of their environmental setting (Table 1) and this provides the reference point for subsequent descriptions in this chapter.

Some tufa deposits occur where deep hydrothermal flow resurges, commonly in association with faults. Due to the absence of associated assemblages of deposits, these tufas would likely be classified in the perched spring-line model. Examples include the deposits at Matlock Bath, Derbyshire, UK (Pentecost, 1999). As with speleothems, growth couplets have been identified as representing annual seasonality (Andrews and Brasier, 2005), which offer the potential for palaeoclimatic and palaeoenvironmental interpretation (section 6). An unusual non-biogenic occurrence of tufa occurs in ultramafic rocks in northern Oman, where hyperalkaline groundwaters precipitate tufa (Clarke and Fontes, 1990).

Pentecost and Viles (1994) classify tufa as a form of travertine and they distinguish between meteogene and thermogene travertine on the basis of the source of the carbon dioxide (soil and deep crustal sources respectively). Thermogene travertine is associated with volcanic centres, high carbon dioxide discharges and high geothermal gradients (section 3.5). Pentecost and Viles (1994) presented a further classification for thermogene travertines, subdividing: spring (fissure ridge or mound, including those of saline lakes) river (cascade, cemented rudites and barrages) and lake deposits (crusts).

Model	Deposits
Perched springline. (resurgences part way up slopes).	Proximal: dominated by liverworts and bryophytes; colonisation by cyanophytes and diatoms. Distal: Fine intraclast tufa and microdetrital tufa.
Cascade.	Curtains of moss associated with waterfalls. Notable absence of upstream lake sediment and biotal associations.
Braided fluviatile.	Braided cyanolith-dominated deposits comprising oncoids and micro-detritus.
Fluviatile barrage.	Phytoherms that obstruct stream flow forming barrages with associated upstream lake sediment and biotal associations.
Lacustrine.	Macro- and microphytes that characterise lake margins; stromatolite, oncoid and intraclast tufas characterise the shallow water and micro-detritus the marginally deeper water.
Paludal.	Surface coatings of tufa on vegetation in marshy localities, where resurgences occur on poorly drained slopes or alluvial valley bottoms.

1 Table 1. Classification of tufa based on environmental setting (Pedley, 1990).

2 An outcome of an investigation of calcretes and speleothems in deep time (Brasier, 2011)
3 was the observation that the relative absence of biogenic soils prior to the evolution of
4 vascular plants implies that different processes were associated with the deposition of
5 terrestrial carbonates during the Archaean, Proterozoic, Cambrian, Ordovician and Silurian.
6 Accordingly, Brasier (2011) has suggested that the term tufa cannot really be applied to deep
7 time; instead, more descriptive classifications, e.g. spring carbonate, stream carbonate and
8 lacustrine carbonate may be more appropriate.

9 **2.3 Carbonate cements**

10 A range of clastic sediments can be cemented, but coarser sediments contain larger pore
11 spaces, which allow thicker cement rinds to form and render them more favourable for
12 research purposes. Detailed petrological descriptions facilitate classification on the basis of
13 vadose or phreatic cementation. A good case study by Strong et al. (1992) described the
14 range of vadose fabrics associated with the cementing of glacial gravels in North Yorkshire,
15 England, UK. This case study also includes a description of some of the terms used to
16 describe pedogenic carbonates, including rhizocretions (the tubiform cements that form
17 around plant roots). Additional pedogenic forms (Tucker, 2011) include duricrusts (lithified,
18 pedogenic surface layers), laminated layers and vadoids (laminated spherical grains that are
19 commonly biologically mediated).

20 **2.4 Pedogenic carbonate**

21 These carbonates primarily occur in arid, semi-arid, or subhumic climates and can be
22 classified on the basis of either morphology or formational process. Irrespective of climatic
23 conditions, formational processes can be subdivided into: per descensum, per ascensum, in
24 situ and biogenic models (Curtis, 2002).

1   **2.5 Third order deposits**

2   Regional lowering of groundwater levels can induce dissolution of secondary carbonate
3   cements. Given their topographical setting, cascade tufa deposits are particularly vulnerable
4   to this form of weathering. However, active dissolution can also result in saturation and
5   supersaturation of the infiltrating water with a potential for re-precipitation, particularly in
6   association with biological mediation. Typical of this process are the third order speleothem
7   deposits observed in the Via Gellia, near Cromford, Derbyshire, UK, which take the form of
8   micro-stalactites (Figure 4) and flowstone. Similarly, inundation of calcareous aeolianites is
9   often characterised by vertical piping because dissolution occurs where percolation is
10   guided by tree roots (Ford and Williams, 2007).
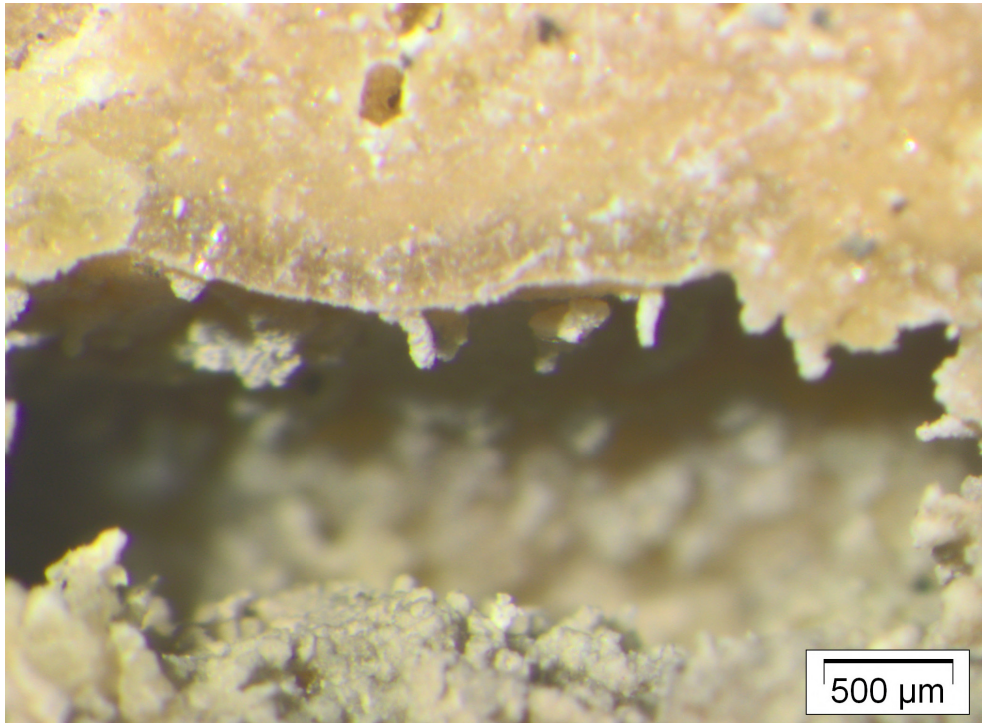
11
12   Fig. 4. Micro-scale third order speleothems in tufa in the Via Gellia, near Cromford,
13   Derbyshire, UK. Larger examples also occur. Binocular microscope image: the British
14   Geological Survey Mineralogy and Petrology Laboratories.

15   **3. Depositional processes associated with secondary carbonate precipitation**

16   Secondary carbonates result from a carbonate source-pathway-receptor system that operates
17   at or very close to the Earth's surface. This generally involves dissolution of an existing
18   deposit of calcium carbonate followed by transport of the dissolved species via surface and
19   groundwater flow paths to a point of precipitation. Favourable conditions for precipitation

1   include supersaturation with respect to calcium carbonate and sites where the physical
2   perturbation of water promotes carbon dioxide outgassing.

3   **3.1 Hydrogeochemistry**

4   The hydrogeochemistry of secondary carbonate deposits is fundamental to understanding
5   their formation. The following comprises a brief overview of the carbonate system. The
6   interested reader is recommended to refer to additional texts, including: Ford and Williams
7   (2007) and Kehew, (2001), as well as the other references cited.

8   Limestone dissolution has been studied extensively in the context of karst geomorphology
9   (Appelo and Postma, 2005; Ford and Williams, 1989 and 2007; Gunn, 1986). The controlling
10 chemical equations with respect to the dissolution of calcium carbonate are:

11 $$CO_2(g) \leftrightarrow CO_2(aq) \tag{1}$$
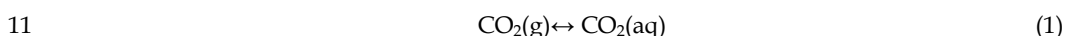
12 This equation represents the absorption of carbon dioxide in water. At equilibrium, the
13 activity of dissolved carbon dioxide is proportional to the partial pressure of carbon dioxide
14 in the gas phase in contact with the aqueous phase containing the dissolved carbon dioxide.
15 Atmospheric Pco_2 is $10^{-3.5}$ atm., whereas the Pco_2 values for groundwater are typically an
16 order of magnitude higher (up to approximately 6%, Ford and Williams, 2007), as a
17 consequence of the addition of biologically (plant respiration) derived carbon dioxide
18 (Atkinson, 1977). The variation in the production of carbon dioxide is primarily related to
19 the temperature, moisture content and amount of organic matter in the soil and therefore it
20 reflects climate and seasonality (Ford and Williams, 2007; Kehew, 2001).

21 $$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \tag{2}$$
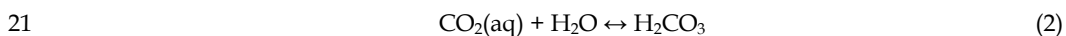
22 Aqueous carbon dioxide dissolves in water to form carbonic acid, which is a weak acid with
23 a potential for dissociation. The theoretical assumption is that all of the CO_2 occurs as
24 carbonic acid, whereas in practice, most of the CO_2 is present as dissolved CO_2. The reaction
25 between aqueous CO_2 and water is slow compared to reactions involving H_2CO_3, thus it
26 becomes rate limiting (Kaufmann and Dreybrodt, 2007). Carbonic acid is a diprotic acid, i.e.
27 it can dissociate twice:

28 $$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{3}$$

29 $$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{4}$$
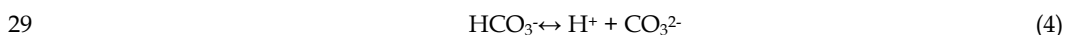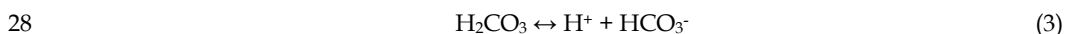
30 The three inorganic carbon species that result from the dissolution of carbon dioxide in
31 water are active over differing pH ranges: H_2CO_3 predominates in acid conditions (pH 1 to
32 6.4); at pH 6.4 the activities of HCO_3^- and H_2CO_3 are equal; from pH 6.4 to 10.33 HCO_3^- is
33 more active; at pH 10.33 the activities of HCO_3^- and CO_3^{2-} are equal, with CO_3^{2-} being most
34 active where the pH exceeds 10.33.

35 Additional hydrochemical factors to be considered in the context of limestone dissolution
36 include: (i) The common ion effect, whereby a common ion derived from the dissolution of a
37 more soluble mineral will reduce the solubility of the less soluble mineral, e.g. the addition
38 of sodium bicarbonate to a solution in equilibrium with calcite would cause an increase in
39 the saturation index for calcite, thereby resulting in calcite precipitation. (ii) Incongruent

1　dissolution, which can occur because of the differing activities of minerals at different
2　temperatures or as a consequence of differing reaction rates. An example of the former is the
3　incongruent dissolution of dolomite and simultaneous precipitation of calcite as a
4　consequence of the common ion effect imparted by anhydrite, which results in
5　dedolomitization (Bischoff et al., 1994). (iii) Increases in ionic strength, which cause
6　reductions in activity coefficients and consequential increases in solubility.

7　Dissolution in karst environments (karstification) can result in surface lowering or an
8　increase in the underground permeability. Rates of dissolution can be calculated from the
9　product of the discharge volume and solute (calcium carbonate) concentration. Both ground
10　surface and underground dissolution are not uniform processes. Dissolution is greatest: at
11　points of convergence where mixing corrosion can occur; in zones of more intense biological
12　activity; where soil moisture is high, and in areas with a sunny aspect (Ford and Williams,
13　2007). As a consequence, dolines can become the focal point for higher rates of surface
14　dissolution. In the UK, dissolution rates of 83 m^3 km^2 a^{-1} have been quoted for Derbyshire
15　and Yorkshire (with 0% and 50% respectively being derived from underground sources;
16　Pitty, 1966 and Sweeting, 1966). A rate of 69 m^3 km^2 a^{-1} was measured by Gunn (1981) for
17　Waitomo, New Zealand (37% from the soil profile and the remainder from up to 5- 10 m of
18　bedrock) where the epikarst is better developed than Derbyshire and Yorkshire. Any
19　assumption of 100% surface lowering is likely to be in error. More recent developments in
20　the understanding of carbonate dissolution, in particular that of kinetic thresholds (see
21　below) and the importance of flow convergence, suggest that an underground component
22　should be expected in all environments. Ford and Williams (2007, p82) note that "*hundreds of*
23　*studies of solutional denudation have been completed since 1960. A major shortcoming of much of the*
24　*work is that autogenic rates have often not been distinguished from mixed autogenic-allogenic rates*
25　*so that there is still no unequivocal answer to the question posed long ago by climatic*
26　*geomorphologists: in which climatic zone does karst evolve most rapidly?*"

27　Initial openings in unconfined karst settings are slowly enlarged by groundwater that is
28　close to saturation with respect to calcium carbonate. The routes conducting the highest
29　discharge are subject to greater dissolution (Palmer, 1991, 2002). Consequently, conduit
30　development is enhanced by larger initial openings and increased hydraulic gradients such
31　that conduit initiation is commonly attributed to base level lowering, which may be a
32　consequence of uplift. For a given partial pressure of carbon dioxide, the initial rate of
33　dissolution decreases in an approximately linear manner with increasing calcium carbonate
34　content, but at 60-90% saturation the dissolution rate decreases rapidly (the kinetic
35　threshold). Whilst the slow uniform dissolution that delays the final stage of saturation with
36　respect to calcite facilitates the gestation of long conduit flow paths and enables deeper
37　penetration of nearly saturated water, it may inhibit supersaturation with respect to calcite.
38　Whereas flow in pre-dissolutional openings is laminar, as dissolution proceeds and openings
39　are enlarged to the hydrodynamic threshold (generally considered to be 10 mm, Fetter, 2001),
40　turbulent flow develops and the rate of carbonate rock dissolution increases rapidly as
41　circulating water becomes less saturated. The hydrodynamic threshold also coincides with the
42　kinetic threshold and the onset of clastic sediment transport, which further contributes to
43　dissolutional enlargement (White, 2002). The rate of dissolution increases with discharge until
44　a maximum is achieved. Flooding increases flow rates and flood water is generally more
45　aggressive being characterised by a lower pH and lower concentration of calcium. During

1   flooding, additional flow paths will be activated, both in the vadose and the phreatic zones,
2   facilitating rapid dissolution and increasing the efficiency of the system.

3   Even without topographical and hydrological focusing of flow, limestone dissolution would
4   be non-uniform because some limestones have a greater propensity for dissolution than
5   others. For example, dissolutional activity (speleogenesis) tends to focus on inception
6   horizons (Lowe, 2000; Banks et al., 2009). Typically, inception horizon-guided dissolution
7   focuses on incipient physical, lithological, or chemical differences that form a focal point for
8   conduit gestation. These differences include: breaks in sedimentary style or bedding;
9   variation in trace chemistry; fossil bands, or contrasts in permeability (e.g. boundaries
10 between limestone and chert, shales or clays). Given sufficient residence time, rock-
11 groundwater interaction ensures that the groundwater chemistry reflects the chemistry of
12 the host geology. Thus inception horizons may also form a source of calcium carbonate,
13 despite the fact that the rates of dissolution quoted above suggest that conduit sources
14 generally provide less than 50% of the dissolved calcium carbonate in a catchment.

15 Other sources of calcium carbonate include soils, superficial deposits and a range of
16 anthropogenic materials. Soil and superficial deposits derived from limestone terrains can
17 contain a significant proportion of leachable calcium carbonate. Typical artificial sources of
18 carbonate with a greater propensity for dissolution include former waste tips resulting from
19 lime processing, quarrying or mining. For example, the source of the artificial tufa barrages
20 in Brook Bottom (Figure 5), which are in the order of 1 m high (Ford and Pedley, 1996), and
21 the source for a nearby, rapidly accumulating speleothem in Poole's Cavern, near Buxton,
22 Derbyshire, UK   (Baker et al., 1999) comprises waste heaps related to the former lime
23 manufacturing industry (Figure 6). The formation of pedogenic carbonate with carbonate
24 derived from artificial sources such as slag, construction materials and cement has been
25 described by Manning (2008).
26

Locality	Secondary carbonate deposit type	Rate (mm/annum)	Reference and notes
Caves of Niue Island, South Pacific.	Speleothem	0.23-0.34	Aharon et al., 2006.
Lathkill Dale, Peak District, Derbyshire, UK.	Tufa	2.5	Andrews et al., 1994. Holocene accumulation rate.
Poole's Cavern, Peak District, Derbyshire, UK.	Speleothem	2.1 – 5.0	Baker et al., 1999. Associated with former lime kilns. 1910 – 1996.
Palaeozoic caves of Wallonie, Belgium.	Speleothem	0.5 – 2.17	Genty and Quinif, 1996.
Malham Tarn, North Yorkshire, UK.	Tufa	0.01-1.30	Pentecost, 1978.
Goredale Beck, North Yorkshire, UK.	Tufa	1-8	Pentecost, 1978.
Mato Grosso, Brazil.	Speleothem	0.012	Soubiès et al., 2005. Variable growth rate.

27 Table 2. Examples of secondary terrestrial carbonate accumulation rates.

1   The precipitation of calcium carbonate can be summarised by:

2    $$Ca^{2+} + 2\ HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O \tag{5}$$
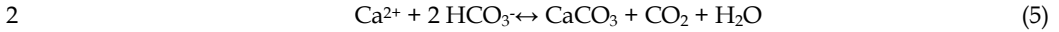
3   A state of supersaturation is required for carbonate precipitation. This can be brought about
4   by the degassing of calcium carbonate enriched waters (Chen et al., 2004; Lorah and
5   Hermon, 1988) that may be associated with cooling and physical or biological degassing of
6   carbon dioxide, reducing the amount of calcium carbonate that can be held in solution. A
7   further process leading to supersaturation is that of evaporation, which is considered to be
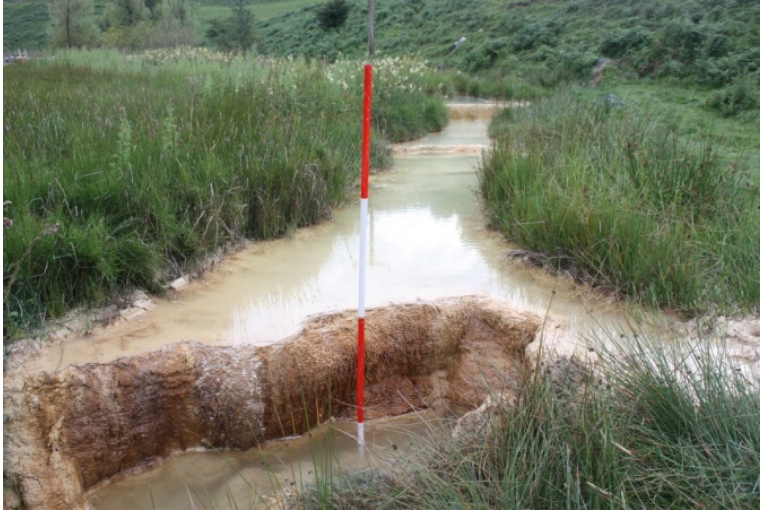
8
9   Fig. 5. Anthropogenic tufa barrages, Brook Bottom, Derbyshire, UK.

10
11   Fig. 6. Cemented lime kiln waste, Brook Bottom, Derbyshire, UK.

the cause of tufa precipitation near many cave and mine entrances (Ford and Williams, 2007). However, a solution that is supersaturated with calcium carbonate does not necessarily give rise to carbonate precipitation if appropriate nucleation sites are not present. Rates of carbon dioxide out-gassing can exceed rates of calcium carbonate precipitation resulting in supersaturation, with a potential to mask any groundwater mixing effects (Thrailkill, 1968). In the case of speleothems, where there is a lower partial pressure of carbon dioxide in the cave atmosphere than in the incoming water, degassing of carbon dioxide leads to supersaturation and consequential precipitation of calcium carbonate.

Accumulation rates for secondary terrestrial carbonates can provide valuable information with respect to landscape evolution. The relatively rapid accumulation rates are such that measurements can be determined in mm per year; examples are presented in Table 2.

3.2 Biological mediation

The nature and extent of biological mediation (enabling) of secondary carbonate precipitation reflects the physical setting of the deposit. Various microbes, flora and fauna contribute to tufa deposition. Cyanobacteria are usually the dominant microbial component (their calcification being associated with the mucopolysaccharide) in fast-flowing streams supersaturated with respect to calcite, where sheath encrustation is the dominant form of calcification (Riding, 2000). Cyanobacteria mineralization is extensively associated with tufa precipitation (Andrews and Brasier, 2005; Brasier et al., 2011; Pentecost, 1988). Photosynthesis causes alkalinization, while exopolymeric substance (EPS) acts as binding site for calcium (less so in freshwater tufas; Dittrich and Sibler, 2010) and the consequential focus for calcium carbonate precipitation. Similarly, microbes are also present in many cave systems, varying between the twilight and aphotic zones of caves (Jones, 2010). They include a diverse range of algae, actinomycetes, bacteria, fungal hyphea and cyanohycea. Cave microbes contribute to the destructive (dissolutional substrate breakdown, boring and degradation) and constructive processes (trapping and binding of detrital particles, calcification and precipitation) that influence the growth of speleothems (Jones, 2010). Evidence of these processes comes from the presence of fabrics (e.g. microbial stromatolites), mineralized microbes and geochemical markers (e.g. lipid biomarkers; Jones, 2010). Cave microbial processes reflect the habitat, particularly the light distribution.

When microbes are encrusted and replaced by calcite, they become part of the substrate. This process results in a range of calcite crystal forms, in both tufas and speleothems. Biomineralization is associated with: bacterial cells, including picocyanobacteria (unicellular cyanobacteria with a cell diameter of 0.2 to 2.0 µm); sheaths, and EPS. Biogenic mineralization can occur through either biologically controlled or biologically induced processes (González-Muñoz et al., 2010). Biologically controlled mineralization occurs in isolated compartments within a living organism, resulting in highly ordered mineral structures (González-Muñoz et al., 2010), which are more typical of shells, but uncommon in bacteria. Biologically induced mineralization is the result of microbial metabolism. There are two stages involved: firstly, active modification of the physical chemistry in the environment of the bacteria leading to an increase in ion concentration (supersaturation; equations 6 to 7); secondly, nucleation of mineral (equation 7). Homogeneous nucleation requires a higher degree of supersaturation, whereas heterogeneous mineralization results from nucleation on bacterial cell walls, bacterial EPS or the new mineral phase (González-

1　Muňoz et al., 2010). The geochemical equations involved in bacterial ion concentration
2　(González-Muňoz et al., 2010) can be summarised as:

3
$$HCO_3^- + H_2O \rightarrow (CH_2O) + O_2 + OH^- \tag{6}$$
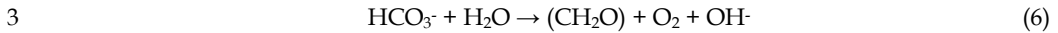
4　This equation represents the photosynthetic bacterial conversion of bicarbonate into reduced
5　carbon. Similar effects can be produced by bacteria that produce ammonia by oxidative
6　deamination of amino acids. Where carbon dioxide is generated by the bacterium,
7　supersaturation with respect to bicarbonate or carbonate may result (González-Muňoz et al.,
8　2010).

9
$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{7}$$
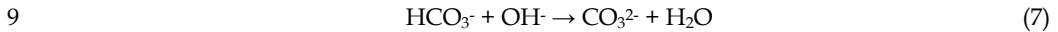
10　Equation 7 results from the exchange of intracellular hydroxide ions for extra cellular
11　bicarbonate ions across the cell membrane. Alkalinization around the bacterial cells induces
12　carbonate generation.

13
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{8}$$

14　Equation 8 represents the precipitation of calcium carbonate on the cell surface. Calcium
15　carbonate may first be precipitated as vaterite. Evidence for a two phase process in active
16　tufa deposition in the Via Gellia, Derbyshire, UK, can be seen in Figures 7 to 9. However,
17　different cyanobacterial species exhibit different calcification fabrics (Pentecost, 1991).
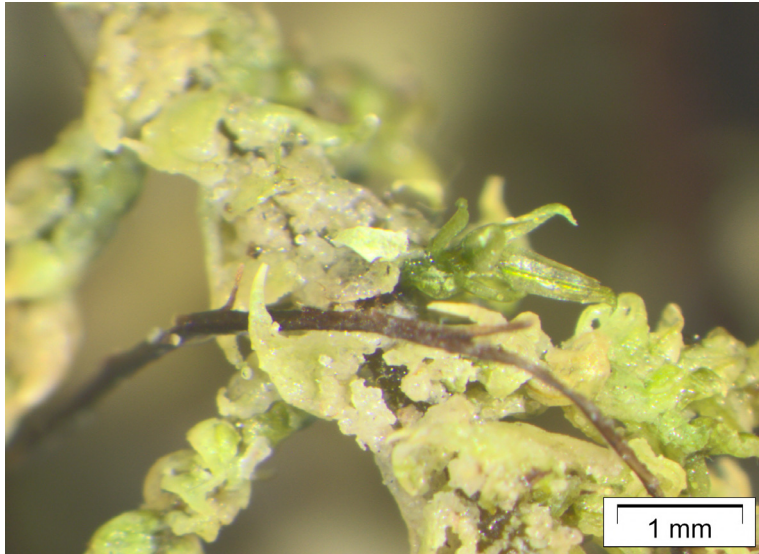
18
19　Fig. 7. Active tufa precipitation in the Via Gellia, Near Cromford, Derbyshire, UK. Binocular
20　mircroscope images: the British Geological Survey Mineralogy and Petrology Laboratories.

21　Dittrich and Sibler (2010) analysed and modelled the functional groups of extracellular
22　polysaccharides of three picocyanobacteria establishing the presence of five to six surface
23　sites, corresponding to: carboxyl, phosphoric, sulphydryl, amine phenol, and hydroxyl

1   groups. The carboxyl and carboxyl-phosphoric groups dominated in all strains, closely
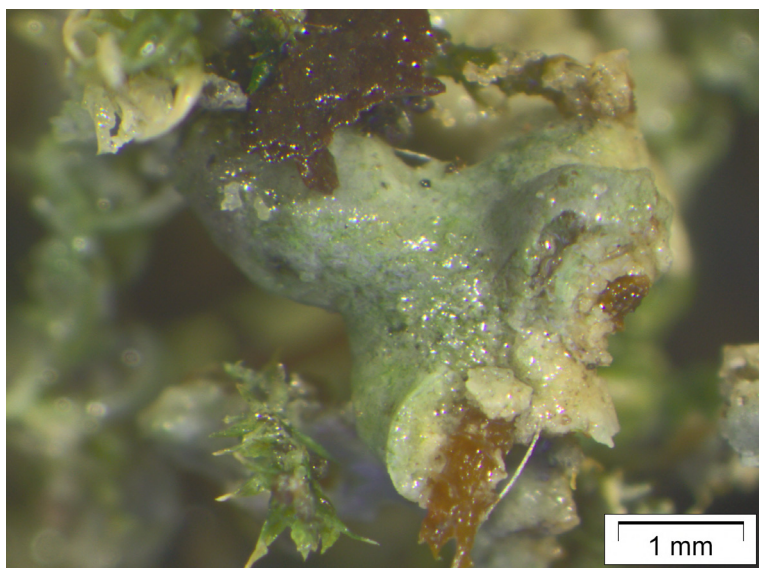2   followed by the hydroxyl groups. Polysaccharides were found to be negatively charged at a
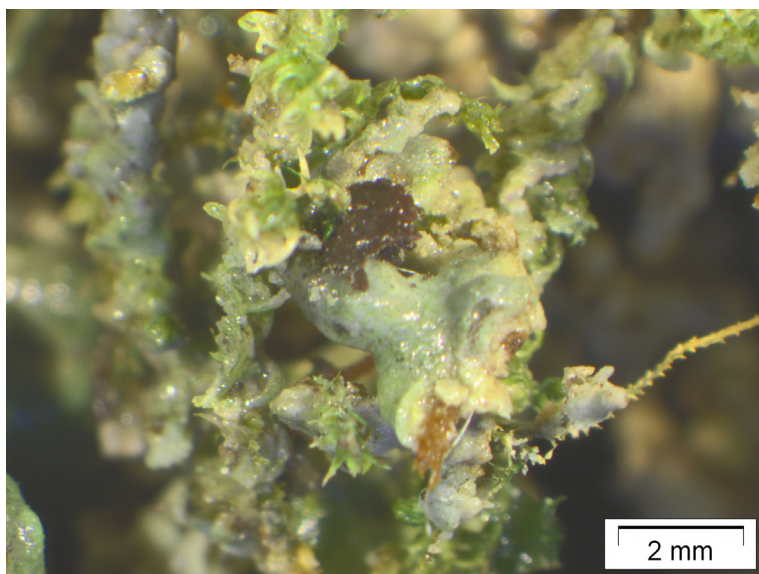
3
4   Fig. 8. Active tufa precipitation in the Via Gellia, Near Cromford, Derbyshire, UK. Binocular
5   microscope images: the British Geological Survey Mineralogy and Petrology Laboratories.


6
7   Fig. 9. Active tufa precipitation in the Via Gellia, Near Cromford, Derbyshire, UK. Binocular
8   microscope images: the British Geological Survey Mineralogy and Petrology Laboratories.

1   pH range of 6 – 7. Therefore, calcium ions can easily be attracted to them. However, removal
2   of calcium reduces the degree of saturation, thereby inhibiting calcium carbonate
3   precipitation. The presence of the carboxyl groups offers the potential to remove metals,
4   thereby overcoming the inhibition to calcium solubility resulting from the presence of low
5   concentrations of metals (Terjesen et al., 1961; Dittrich and Sibler, 2010). Decomposition of
6   the EPS releases bicarbonate and calcium ions, which increases the calcium carbonate
7   saturation state and promotes precipitation.

8   **3.3 Geomorphological and tectonic mediation**

9   A number of deposits are representative of specific geomorphological and tectonic settings,
10 as acknowledged in Pedley's (1990) classification of tufas (section 2.2) and as evident in the
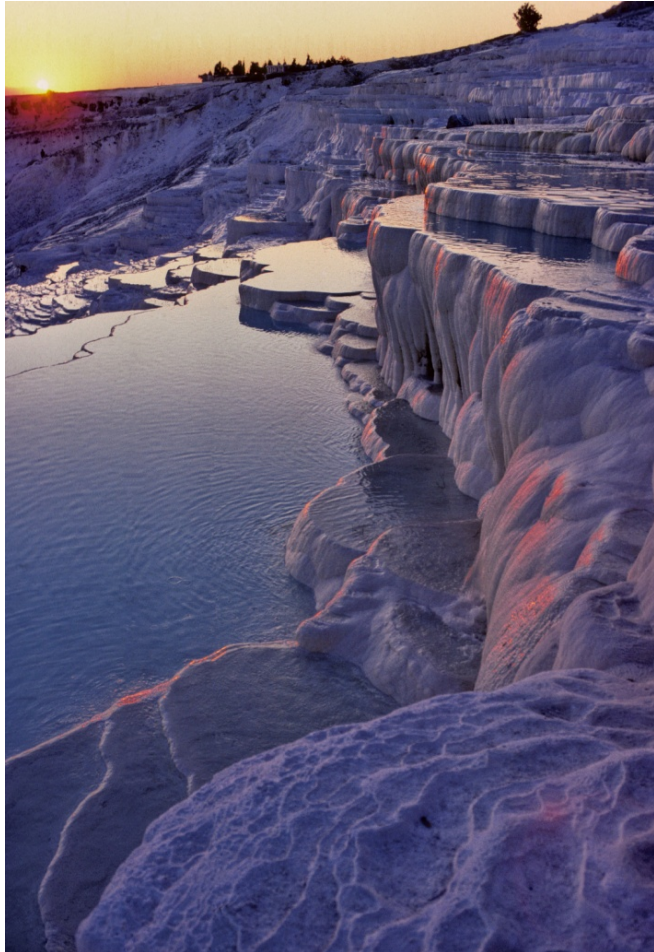
11
12 Fig. 10. Pamukkale Travertine, SW Turkey. Photograph: Anthony H Cooper, British
13 Geological Survey.

1   Antalya area of south-west Turkey, where tufa terraces have been related to glacio-eustatic
2   sea level change (Glover and Robertson, 2003). Similarly, Forbes et al. (2010) described a
3   number of tufa deposits in the south-western coastal zone of Western Australia. These
4   deposits are characterised by cascade to barrage pool and perched spring line to barrage
5   pool situations, which are associated with coastal waterfall and supratidal
6   geomorphological settings respectively. Geomorphology and tectonic setting can also
7   influence the carbonate source and flow paths through uplift and erosion. As an example, a
8   rock slide in the Fern Pass, Austria produced carbonate rock flour which formed the
9   carbonate source for subsequent cementation of the rockslide breccias (Ostermann et al., 2007).
10 As thermal deposits, travertines are also likely to be moderated by tectonic events, particularly
11 given that the location of these deposits is commonly related to faults (Pentecost, 1995).
12 Similarly, fissure ridge travertine deposits, associated with listric faulting in the Gediz Graben
13 extensional province of Turkey have been explained by their tectonic setting (Selim and Yanik,
14 2009). The Pamukkale travertine (Figure 10) in Turkey occurs in a different extensional tectonic
15 regime (Selim and Yanik, 2009; Şimşek, 1993). In the case of the Lapis Tiburtinus travertine,
16 Central Italy, travertine cycles reflect water table fluctuations associated with fault and
17 volcanic activity between 115 000 and 30 000 BP (Faccenna, et al., 2008).

18 **3.4 Anthropogenic influences**

19 As well as providing artificial sources of calcium carbonate, anthropogenic influences can
20 affect flow paths and the depositional rates of secondary carbonates that are commonly
21 encountered in infrastructure, mines and industrial areas. The growth of speleothems has
22 been reported in a number of such settings, e.g. railway arches and disused water reservoirs.
23 Recent work in opening the disused railway cuttings between Buxton and Bakewell in the
24 White Peak, Derbyshire, UK, has exposed occurrences of speleothems, flowstone and tufa
25 associated with the engineered structures, including tunnels, bridges and cuttings.
26 Occurrences of this kind may be a consequence of either the opening of new flow paths, or
27 the interception of pre-existing ones, as observed in a cutting (Figure 11) where tufa
28 precipitation is clearly associated with water discharging from exposed inception horizons.
29 Flow rates associated with these deposits are generally low, with flow commonly occurring
30 as minor seepages in the unsaturated zone. The nature of anthropogenically mediated
31 secondary deposits would appear to reflect the significance of biological mediation, with tufa
32 forming in moist locations where mosses and bryophytes establish themselves, commonly
33 associated with shade and good ventilation. As the majority of the engineered structures can
34 be dated, secondary carbonate deposits in these settings provide an opportunity for assessing
35 minimum rates of precipitation. Cemented kiln waste encountered in Brook Bottom,
36 Derbyshire, U.K (Figure 6), provides further evidence for the occurrence of anthropogenically
37 moderated calcite precipitation. Underground, rapid rates of calcium carbonate precipitation
38 are implicit in the occurrence of tufa deposits above a skeleton discovered in historic mine
39 workings in Lathkill Dale, Derbyshire, UK in 1744 (Rieuwerts, 2000).

40 Anthropogenic influences have been linked with a range of factors that may have
41 contributed to the post-Holocene decline in tufa deposition (Goudie et al., 1993), which in
42 Derbyshire, UK, primarily occurred approximately 4000 years BP. This coincides with
43 Neolithic to Early Bronze Age deforestation (Taylor et al., 1994), which may have influenced
44 barrage type (section 2.2) tufa deposition in one or more of the following ways (Goudie et
45 al., 1993): reduced availability of carbon dioxide in the vicinity of areas of groundwater

recharge; less woody material available to form dams; induced soil erosion, associated with further reductions in the availability of carbon dioxide; alteration to the shade causing stress to mosses or cyanobacteria at resurgences; increased access for grazing with consequential changes to groundwater chemistry, including eutrophication, and turbidity, thereby inhibiting the bacteria and mosses responsible for tufa accumulation, and increased surface run-off causing increased turbidity and dissolution potential during periods of high discharge. Tufa formation is severely limited when the mean annual air temperature falls below 5^0C (Pentecost, 1996; Pentecost and Lord, 1988), which suggests that a component of the late Holocene decline may be associated with lower mean air temperatures.

Fig. 11. Tufa formation below an inception horizon in a railway cutting between Buxton and Bakewell, Derbyshire, UK. 1 m length of tape measure for scale.

3.5 Travertine forming processes

Pentecost (1995) summarised the distribution of Quaternary thermogene travertine formations in Europe and Asia Minor. Of the 93 sites identified, 56 are known to be active and many of the European deposits date to the Pleistocene or late Pliocene. A significant proportion of the active sites occur in Italy and Turkey, where they correspond with volcanic centres and high carbon dioxide discharges, associated with high geothermal gradients. The precise relationship between volcanism and travertine formation has yet to be established. On the basis of isotope analyses, it has been hypothesised that carbon dioxide enriched fluids derived from the upper mantle and from limestone decarbonation dissolve sedimentary carbonate (Pentecost, 1995). However, in the case of the Lapis Tiburtinus travertine, Tivoli, Central Italy, carbon isotope analysis of the travertine suggests

a hydrothermal origin for the fluids that precipitated the tufa (Faccenna et al., 2008). The majority of hydrothermal springs rise on faults (Pentecost, 1995). The largest depositional region extends from Greece, through Turkey and across the Caucasus Mountains into Russia, where convergence of the Eurasian and Afro-Arabian plates is believed to be responsible for the recent volcanism and hot spring activity.

3.6 Diagenesis

Diagenesis of carbonate sediments can occur through cementation, dissolution, microbial micritization or neomorphism. The metastable condition of many carbonate minerals, such as aragonite, renders them susceptible to recrystallization. Potentially, this may result in changes that cause the deposits to be less useful for interpreting climate change or depositional environments. Recrystallisation may occur through changes to the isotopic signature or fractionation of elements used for dating. Thus, understanding of diagenetic processes is important. MartÍn–García et al. (2009) demonstrated this in the case of speleothems from the Castaňar Cave, in the southern part of the Iberian Massif in Spain. Here speleothems in dolomite hosted karst were found to have undergone micritization and neomorphism thereby modifying the primary features including the stable isotope, strontium and magnesium contents. Similarly, in a study of the diagenesis of aragonite in speleothems in Korea, Woo and Choi (2006) found that aragonite inversion to low magnesium calcite was associated with the remobilisation of stable isotopes and trace elements, with a notable difference in the carbon isotope signature.

In contrast, in a petrographic examination of Greek tufa deposits with a significant development of sparite over micrite, the relative absence of diagenetic processes was established (Brasier et al., 2011). This disproved a formerly held view that the extent of sparite was likely to be a secondary feature (diagenetic aggrading neomorphism, e.g. Love and Chafetz, 1988) of the tufa. The study of the distribution of sparite and micrite in two Greek Pleistocene tufa stromatolites (Brasier, et al., 2011) revealed primary columnar calcite spar in a younger deposit (ca 100 ka) from Zemeno occurring immediately above chironomid larval tubes with which its growth was associated, whilst an older tufa (ca 1 Ma) from Nemea comprised proportionately more sparite with some chironomid tubes and cyanobacterial filaments. Comparison of stable isotopic trends (section 5.2) revealed that both deposits supported resolvable seasonal responses, suggesting that there had been limited post-depositional alteration of either tufa. The higher proportion of sparite in the Nemea deposit has been attributed to abiotic, speleothem-like growth of near hemispherical laminations from thin films of water (Brasier et al., 2011).

4. Spring and cave drip geochemistry

The use of seasonal signatures derived from carbonate deposits, particularly as a source of high-resolution palaeoclimate data, drives the need to understand how this is expressed in the supply waters. Spring geochemistry is of interest to the research of secondary terrestrial carbonate deposits, because it reflects the source of the carbonate as well as the processes operating during transport of the solutes between the points of dissolution and precipitation. Drip and cave air geochemistry is of equivalent interest in the case of cave deposits (Baldini et al., 2006). Calibration of speleothem oxygen isotopes in current calcite deposits at Tartair cave, Sutherland, North West Scotland with the oxygen isotope

1 signatures of precipitation and percolating waters (Fuller et al., 2008) demonstrates the
2 benefit of speleothem research to climate studies.

4.1 Flow path geochemistry

4 Groundwater can be characterized by the degree of equilibrium between the water and the
5 wall rock (Drake and Harmon, 1973; Richardson, 1968; Shuster and White, 1971, Smith and
6 Atkinson, 1976). Factors that influence flow path geochemistry include: flow-through time
7 (water-soil contact or water-rock contact time); atmospheric conditions, including
8 temperature; thickness and type of superficial cover; bedrock geology, and epikarst
9 thickness. These variables are reflected in the range of proposed classifications, based on:
10 individual parameters, ratios of parameters (Downing, 1967 and Vervier, 1990), flow-
11 through times, as indicated by hardness and P_{CO_2} (Drake and Harmon, 1973; Pitty, 1966),
12 seasonal variation of parameters (Shuster and White, 1971) and variation with discharge
13 (Jacobson and Langmuir, 1974). Kehew (2001, p. 16) suggested, "*By knowing the state of*
14 *equilibrium between the water and minerals within the aquifer, we can predict the type of reactions*
15 *that are occurring or would be likely to occur*", but it is rarely possible to sample a karst system
16 along its flow path, instead use is made of springs and geochemical modelling to assess the
17 likely processes within the system.

18 Conceptually, speleothems form within a flow path, thereby providing information on flow
19 path geochemistry in the vadose zone. It has been established that the five main controls on
20 their growth rates are: drip rate, activity of calcium in the drip water, air temperature, cave
21 air P_{CO_2} and film thickness (Fairchild et al., 2001). In this context, cave drip water chemistry
22 and cave air chemistry is important for understanding the hydrological controls on
23 speleothem growth rates. This has been demonstrated in studies of hourly resolved cave
24 P_{CO_2}, and cave drip water hydrochemical data, in Crag Cave, SW Ireland (Baldini, et al.,
25 2006; Sherwin and Baldini, 2011; Tooth and Fairchild, 2003). These studies demonstrated
26 that calcite deposition on stalagmites can be moderated by prior calcite precipitation on
27 short timescales. Given relatively constant conditions (air temperature, film thickness and
28 low drip rates) controls on speleothem growth were most strongly influenced by cave air in
29 winter, whilst drip water dilution caused by rain events may play a more significant role
30 during the summer. In a separate study of the same cave system, Tooth and Fairchild (2003)
31 established that some speleothems at this site may record a signal of palaeohydrology
32 determined by variations in Mg/Ca ratios, with higher Mg/Ca ratios indicating lower flow
33 conditions when base flow is maintained by long residence time storage water.

4.2 Spring geochemistry

35 Geochemistry can be used to assess the functioning of karst springs, for instance the
36 degree of equilibrium between the groundwater and the wall rock has been taken as an
37 indicator of the type of flow feeding the spring (e.g. Atkinson, 1977a; Shuster and White,
38 1971; Worthington and Ford, 1995). Shuster and White (1971) classified diffuse and
39 conduit flow waters; Bertenshaw (1981) vadose and phreatic, or open and closed systems,
40 and Worthington (1991) underflow and overflow systems. The terms "open" and "closed"
41 are defined by Appelo and Postma (2005), Ford and Williams (2007), Gunn (1986) and
42 Smith and Atkinson (1976). The open system is one in which gas, water and rock are all in
43 contact with one another such that carbon dioxide is available to replace that used up in

the reaction of limestone and carbonic acid. The closed system is one in which gas and water come into equilibrium, but a replacement supply of carbon dioxide is not continuously available during the reaction between limestone and carbonic acid. There is a gradation between fully open and fully closed systems. In the closed system, the concentration of carbonate species with changing pH is non-linear and less than in open systems. Karst systems are also described as diffuse or focused, which again may be reflected in the spring chemistry. Further understanding of aquifer processes can be derived from the seasonality of spring data.

4.3 Seasonality in spring and groundwater geochemistry

Seasonality in biogenic activity results in fluctuation in the biogenic production of carbon dioxide with a consequential seasonality to the partial pressure of carbon dioxide in infiltrating groundwater. Additionally, maximum evapotranspiration associated with the summer months concentrates constituents entering the ground to as much as twice that measured in the atmospheric precipitation (Edmunds, 1971). The extent to which seasonality is exhibited in spring water chemistry has been the subject of debate, possibly in part due to the method of monitoring (analogue versus digital). Shuster and White (1971) were able to use seasonality as an indicator of flow type in the Central Appalachians. More specifically, they related the variability of total hardness (expressed as a percentage coefficient of variation i.e. standard deviation/mean) to the type of resurgence. Springs with a variability of greater than 10% were interpreted as conduit flow, whilst those with less than 5% as diffuse, or percolation flow. However, in the Central Appalachians the variation in carbon dioxide pressures was more closely related to source areas (Shuster and White, 1971) than to seasonality. Deriving comparable coefficients of variation with respect to total hardness, Jacobson and Langmuir (1974) concluded that discharge was a more important influence on water chemistry than season, particularly for dispersed recharge type springs. In a more recent study in subtropical areas of SW China, Liu et al. (2007) collected data over two years of continuous monitoring of pH, conductivity, temperature and water stage from two epikarst springs (Nongla and Maolan springs). This was used to calculate partial pressures of carbon dioxide and the saturation indices with respect to calcite and dolomite. The study identified marked seasonal, diurnal and storm-related variations in the monitored and modelled parameters. Coefficients of variation of the parameters indicated that the greatest variation was at the seasonal scale, whilst storm scale exceeded diurnal variation. The variation was marked by higher conductivity and lower pH in the summer and daytime. Co-variation with temperature indicates that this influences the production of carbon dioxide in the soil. High rainfall events mask the seasonality as a consequence of the dilution. Monthly monitoring, over a 5-year period at fourteen localities along a tufa bearing stream on Carboniferous to Permian limestone at Shimokuraida, Niimi City, in southwest Japan, identified seasonal variation in the soil and spring water partial pressures of carbon dioxide. The variation was higher in the summer to autumn and lower in the winter to spring (Kawai et al., 2006).

4.4 Relationships between supply water chemistry and carbonate precipitation

Individual studies have demonstrated how supply water chemistry influences carbonate precipitate geochemistry. For example, the oxygen isotope content of speleothems in Tartair

1 Cave, Sutherland, North West Scotland corresponds with the oxygen isotope signatures of
2 precipitation and percolating waters (Fuller et al., 2008; section 4). Leybourne et al. (2009)
3 demonstrated that rapidly deposited tufa Sr/Ca ratios were controlled by spring water
4 Sr/Ca ratios in a carbonate rock aquifer in the Interlake Region of Manitoba, Canada. They
5 showed that whilst the $\delta^{18}O$ in the tufa is in equilibrium with the water, the $\delta^{13}C$ is enriched
6 compared with the groundwater. In a case study in the Wye catchment, Derbyshire, UK,
7 Banks et al. (2009) defined a number of formationally-based hydrogeological domains.
8 These were derived from the results of dye tracing tests, analysis of water well monitoring
9 and spring geochemistry and established that occurrences of barrage tufa are associated
10 with only one of the domains. The implication was that the inception horizons in this unit
11 provided a source of calcium during tufa precipitation (Banks et al., 2011).

12 **4.5 Stream chemistry**

13 Whilst spring chemistry provides an indication of the functioning of the karst aquifer,
14 stream or river chemistry in karst terrains provides a catchment scale indication of
15 dissolution and landscape erosion. A study of the river geochemistry of the Wujiang and
16 Quingshuijiang rivers in the Guizhou Province of southern China (Han and Liu, 2004)
17 demonstrated that dissolution in the catchments was attributable to both carbonic and
18 sulphuric acids. Isotope studies ($^{87}Sr/^{86}Sr$) and the presence of nitrates indicate an
19 anthropogenic source for a proportion of the sulphuric acid; thereby the implication is of
20 anthropogenically accelerated erosion rates (43 to 49 mm per annum). Given the
21 vulnerability of karst aquifers to contamination (Vesper et al., 2001), which results from the
22 existence of open fast flow paths in the form of conduits, closely spaced monitoring in rivers
23 can provide useful information with respect to point and diffuse sources and sinks of
24 contaminants. A study of this type was undertaken by Banks and Palumbo-Roe (2010) in
25 Rookhope Burn, a lead-zinc mining impacted karst catchment and tributary of the River
26 Wear in northern England. This identified previously unrecognised resurgences of zinc-
27 contaminated groundwater.

28 **5. Geochemistry of secondary carbonate deposits**

29 **5.1 Secondary carbonate geochemistry**

30 Secondary carbonate cements formed by meteoric water are representative of the local
31 environmental conditions at the time of precipitation. Speleothems form in the vadose
32 (unsaturated) zone by water dripping from the ceilings or walls of caves or from the
33 overhanging edges of rock shelters. The precipitation of calcium carbonate is caused by the
34 degassing of carbon dioxide into the cave, resulting in supersaturation of the groundwater
35 with respect to calcium carbonate and consequential precipitation, which may also be
36 biologically mediated. Seasonal lamination may occur as a consequence of seasonal
37 variations in: drip rate (potential for variation in layer thickness); drip water supersaturation
38 with respect to calcium carbonate, and cave climate (temperature, humidity and carbon
39 dioxide concentrations). Lamination thickness measured in Belgian stalagmites by Genty
40 and Quinif (1996) varied both between and within stalagmites, in the range 0.47 to 2.17 mm.
41 Laminae were defined by variations in the density of the intercrystalline pores and
42 inclusions. The pores were elongate parallel to the growth direction with their length
43 ranging from 0.05 to 1 mm. Annual laminations formed as couplets of white porous laminae

1   and dark compact laminae of palisade calcite. The dark laminae, which have a lower pore
2   density, form during periods of moisture excess with insufficient time for surface degassing
3   of carbon dioxide, resulting in run-off and precipitation on the sides of the speleothems.
4   This causes an overall thinning of the laminae and localised widening of the stalagmite.
5   During drier periods, the narrow white porous calcite laminae are attributable to a
6   chemically efficient flow rate that allows sufficient time for carbon dioxide outgassing and
7   precipitation of calcium carbonate at the top of the stalagmite.

8   Annual trace element variation within speleothems, in part attributable to colloid transport,
9   provides valuable information that can be used to investigate climate change. Fairchild et al.
10 (2001) used ion microprobe analyses of speleothems from five western European cave sites
11 to demonstrate seasonality in concentrations of magnesium, strontium, barium, fluoride,
12 hydrogen and phosphorus (as phosphate). The caves studied were: Crag Cave, County
13 Kerry and Ballynamintra, County Wexford in Ireland; Uamh an Tartair, Sutherland,
14 Scotland; Grotte Pere-Noël, Belgium, and Grotta di Ernesto, north-east Italy. It was
15 established that: i) Magnesium, strontium and barium substitute directly for calcium. ii)
16 Magnesium/ calcium ratios reflect the supply ratio, tending to be lower under high flow
17 conditions, because of prior calcite precipitation along the flow path. iii) In cave
18 environments with low sodium and magnesium/calcium ratios, and with a constant
19 temperature, the key variables affecting strontium partitioning are the supply ratio of
20 strontium/calcium and the growth rates, with more strontium being incorporated at higher
21 flow rates. iv) The concentration of sodium and fluoride was found to reflect the growth rate
22 (more sodium and fluoride at higher growth rates) rather than variations in the supply
23 water chemistry, a consequence of the rapid incorporation of these elements, but results in
24 charge imbalance (growth defect) that can be satisfied by the further incorporation of more
25 trace elements and suggests greater concentration of trace elements during periods of rapid
26 speleothem growth.

27 Comparable findings have been made in studies of tufa deposits which also comprise
28 calcium carbonate that is representative of the local environmental conditions at the time of
29 precipitation. This particularly applies to biologically moderated tufas, where the
30 cyanobacteria do not have a direct influence on the rate, mineralogy, or geochemistry of the
31 calcium carbonate that precipitates around them (Andrews and Brasier, 2005). The
32 seasonality of tufas results from cyanobacterial blooms in the early spring, which facilitates
33 nucleation of densely calcified darker layers. As the nutrient supply (diatoms) reduces,
34 cyanobacterial growth slows and filaments aggregate into scattered bundles separated by
35 cavities resulting in a lightly calcified, porous layer (Andrews and Brasier, 2005). Strontium,
36 magnesium and manganese concentrations in summer precipitates have been shown to be
37 higher than those in winter (Chafetz et al., 1991). Magnesium geochemistry is more complex
38 than indicated by Chafetz et al. (1991); as with speleothems, upstream precipitation of calcite
39 has been shown to have a minor effect on magnesium chemistry, and magnesium
40 concentrations appear to be controlled by aquifer processes rather than temperature
41 (Andrews and Brasier, 2005).

5.2 Stable isotopes (carbon and oxygen) – environmental and hydrological implications

44 The ratio of $\delta^{18}O$ to $\delta^{16}O$ measured against a standard gives an indication of mean annual
45 surface temperatures at the time of speleothem precipitation. Similarly, ratios of carbon

isotopes may provide evidence for seasonality. Given no direct contact with the external atmosphere and constant temperature due to the limitation of air circulation, calcite precipitated in the resultant speleothem will form in isotopic equilibrium with the water from which it is precipitated. Changes in surface atmospheric conditions will be reflected in the percolating water and isotopically preserved in the speleothem and any fluid inclusions. However, not all speleothems can be studied in this way. For example, some may undergo diagenesis, or the speleothem may be contaminated by detrital matter (section 3.6).

Associated with the seasonality in tufa precipitation is a $\delta^{18}O$ trend to isotopically heavy winter-time tufa and isotopically light summer-time tufa. This is attributed to changing water temperature. $\delta^{13}C$ also shows seasonality with the summer-time sparry calcite exhibiting lower values than the micritic winter laminae. Matsuoka et al. (2001) suggested that seasonality in $\delta^{13}C$ in their Japanese study was attributable to winter degassing of carbon dioxide from groundwater fed spring water. In winter, the subsurface karst conduit air is warmer and less dense than the atmospheric air, so ventilation of the conduit air decreases the subsurface air P_{CO_2} and causes degassing of isotopically light $^{12}CO_2$ from the groundwater (Andrews and Brasier, 2005).

In a study of Quaternary pedogenic carbonates, designed to assess their usefulness as environmental indicators in Texas, Zhou and Chafetz (2010) undertook stable isotope analyses on a range of host strata. In the Gulf Coastal Plains, the Southern Highland Plains and the west, $\delta^{13}C$ values were found to vary in response to changes between C_4-dominated and C_3-dominated plants. Additionally, $\delta^{18}O$ values of the late Quaternary pedogenic carbonates decreased gradually from east to west, mimicking the spatial variation of $\delta^{18}O$ in modern meteoric water and increased distance from the Gulf of Mexico. However, the stable-isotope values developed on marine limestone and calcareous alluvium in central and southern Texas contained isotopic signatures that were derived from the host strata. These findings imply a variable potential for the interpretation of pedogenic carbonate stable isotope signatures.

5.3 Fractionation of isotopes

Fractionation of isotopes occurs where there is a change to the speleothem drip water chemistry prior to or during precipitation. This may occur in the soil, vadose zone, epikarst or in the cave environment. Potentially, fractionation may result in misinterpretation of isotope analyses. Fractionation effects can be estimated by analysing the variation in hydrogen isotopes, which are unaffected during crystal formation (Lauritzen, 1993). Additional information may be obtained from multi-proxy approaches, including non-conventional isotope systems, such as magnesium fractionation (Immenhauser et al., 2010). Fractionation can also occur as a consequence of post-depositional weathering of secondary carbonate deposits.

5.4 Isotopes and dating of secondary carbonate deposits

Radiometric dating methods are based on the decay of natural radio isotopes with a fixed decay constant (λ) for a given isotopic species. Cosmogenic isotopes are formed through cosmic reactions, e.g. with atmospheric nitrogen to generate carbon-14 (^{14}C), or rocks and

1 soil ([10]Be, ^{14}C, [26]Al and [36]Cl). The application of the appropriate techniques is based on the
2 geochemistry and suspected age of the dateable material. The suspected age is considered
3 because each of the isotopes has a different half-life e.g. 5730 +/- 40 years for [14]C. [14]C ages
4 are generally determined from atom counts undertaken in an accelerator mass spectrometer.
5 The principal dating technique used for secondary carbonate deposits is uranium-thorium
6 dating. Radioactive uranium ([238]U and [235]U) generates daughter isotopes [206]Pb and [207]Pb
7 through radioactive decay (of α, β and γ particles) via intermediate daughter species
8 including [234]U, and [230]Th. Uranium is soluble in carbonate waters; rock weathering results in
9 the preferential removal of [234]U, whereas thorium is far less soluble and bonds preferentially
10 to clay particles. Consequently, whilst [234]U may be incorporated in secondary carbonate
11 cements, thorium will not be represented, thereby enabling dating from the U/Th ratio. For
12 U/Th dating it is necessary that samples contain sufficient uranium with low [200]Pb
13 concentrations. This dating technique has been extensively applied to speleothems (Baker et
14 al., 2008; Richards and Dorale, 2003), tufas (albeit with the difficulty of low uranium
15 concentrations in young tufas, Garnett et al., 2004) and increasingly to cemented rudites
16 (Sharp et al., 2003). In interpreting the results, consideration needs to be given to the
17 potential for sample contamination or for fractionation to have taken place, i.e. whether the
18 system is open or closed to post depositional migration of constituent nuclides (Richards
19 and Dorale, 2003). The use of other intermediate uranium daughter isotopes for dating, e.g.
20 protactinium 231 (Edwards et al., 1987), forms the subject of ongoing research. Another
21 research direction is the use of laser ablation linked ICPMS for determining uranium isotope
22 ratios (Eggins et al., 2005). However, at present the precision of conventional TIMS or solution
23 MC-ICPMS techniques has not been achieved. Other dating techniques include: optically
24 stimulated luminescence (OSL), electron spin resonance (ESR; Grün, 1989) and amino acid
25 racemisation. The latter is obtained from changes to the structure of organic matter, a process
26 that is temperature controlled. Longer established dating techniques include palaeomagnetism
27 (Rowe et al., 1988) and biostratigraphy, using fauna, flora and pollen.

28 Isotopic dating offers the potential for determining the minimum age of the surfaces
29 (geological or anthropogenic) upon which the secondary carbonate deposits lie. For
30 example, critical dating evidence (455 ka BP) has been derived from U/Th dating of tufa
31 overlying an exposure of the Anglian Lowestoft Formation (a glacial till) at a Palaeolithic
32 site at West Stow Suffolk, UK (Preece et al., 2007). At this locality the land snail assemblage
33 identified in the tufa comprised woodland taxa indicative of a wetter and potentially
34 warmer climate than the present day.

6. Secondary carbonate deposits as indicators of palaeohydrogeology, climate change and landscape evolution

6.1 Karstification and secondary carbonate deposition

38 The sources for secondary terrestrial carbonates are of interest to the karst hydrogeologist
39 because of the potential to establish the palaeohydrological conditions at the time of
40 precipitation (section 4.4). The spatial distribution of dissolution is of interest both to the
41 hydrogeologist as an indicator of palaeo flow conditions and to the karst geomorphologist
42 as it contributes to our understanding of landscape evolution.

6.2 Implications for interpreting climate change

The presence or absence of speleothems provides valuable information regarding sufficiency of water supply and soil carbon dioxide for their growth. As their growth is restricted to the vadose zone, they provide constraints on the opening of passages and water table fluctuations (Richards and Dorale, 2003). In the context of glacial-interglacial cycles, speleothem growth is at a maximum during warm periods. It is limited by frozen ground conditions, ice cover and subsequent melting. Frozen ground and lower biogenic carbon dioxide supply limit growth in permafrost conditions (Lowe and Walker, 1997). Growing from meteoric water, speleothems and tufa preserve a continuous record of climate change for the duration of their formation, albeit that this may be moderated by ground storage of the water. If certain conditions are satisfied, speleothems may contain annual laminae, generally of 10 to 1000 µm (Baker et al., 2008). The necessary conditions include: an annual cyclicity of the surface climate (e.g. seasonal monsoon, annual migration of the inter-tropical convergence zone, or a seasonal moisture deficit); a cyclic signal expressed in the speleothem as a consequence of groundwater, or cave atmosphere signal transfer, and a depth of speleothem such that groundwater moderation does not mask the climatic variation (Baker et al., 2008). Thus, detailed studies of annual growth laminae offer the potential to provide evidence of past precipitation, temperature, or atmospheric circulation. This can be done using a number of techniques (Table 3). Annual laminae, which are a function of palaeoclimate, define speleothem growth rate. Warmer, moister conditions are associated with increased growth, except under peat soils where warmer, drier conditions promote growth (Fairchild et al., 2001). Laminations represent a change in chemical composition of the speleothem that can be made visible by imaging or chemical mapping (Baker et al., 2008; Table 3). Visibility of the laminae depends on alternation of the crystal arrangement with a well-defined morphology. In some examples, e.g. Genty and Quinif (1996) there is an alternation between dark compact calcite and white porous calcite.

Providing laminae periodicity can be established and it can be demonstrated that the change in annual lamina thickness reflects surface climate variations through speleothem growth rate and geochemistry, then quantitative reconstruction of climate from stalagmite growth layers, or lamina-climatology (Baker et al., 2008) studies can be undertaken. Using this technique, Genty and Quinif (1996) distinguished 11-year cyclicity in speleothem growth in a pre-Holocene Belgian stalagmite, which they suspected of being linked to sunspot activity. Not all laminae are annual. Sub-annual laminae are more likely to be present in speleothems that grow closer to the ground surface without moderation by groundwater. Investigation of the periodicity of the laminae can be undertaken using: dating techniques; laminae counting between events; drip water chemistry monitoring (including fluorescence) or a comparison of observed with theoretical prediction of lamina width. Attention has also been given to the application of hyperspectral imaging, the opportunity for which lies in the potential to use the near infra-red range to map out areas of stalagmite where fluid inclusions are present. The sensitivity of speleothem growth to local conditions is such that there can be variation in drip chemistry within a single cave system, e.g. Pitty (1966) in Poole's Cavern, Derbyshire, UK. This results from the variation in individual flow paths and the consequential climate filtering, which may give rise to poor correlation between individual speleothems within the same cave system. This difficulty is best overcome using a multi-parameter investigative approach (Baker et al., 2008), e.g. lamina thickness, stable isotope investigation and trace element geochemistry.

Technique	Application	References
Measurement of change in laminae width using conventional transmission and reflected light microscopy on polished and thin sections. Scanning electron microscopy to look at pore spaces.	Speleothems from across the world including, Belgium; Brazil and Ethiopia.	Genty and Quinif, 1996; Soubiès et al., 2005, and Baker et al., 2007.
Studies of trapped pollen.	Speleothems.	McGarry and Caseldine, 2004.
Ratios of stable isotopes.	Speleothems, tufa, cements.	Andrews and Brasier, 2005; McDermott, 2004.
Calcite-aragonite couplets.	Speleothems, examples studied from north-west Botswana and Nepal.	Railsback et al., 1994, and Denniston et al., 2000.
Variations in trace element ratios.	Speleothems.	Fairchild et al., 2001.
Optical luminescence.	Speleothems; examples include Poole's Cavern, Derbyshire, U.K.	Baker et al., 1999.
Hyperspectral imaging used to discriminate laminar density contrasts.	Speleothems; examples studied from north-east Turkey.	Jex et al., 2008.

1   Table 3. Secondary carbonate imaging techniques.

2   Remnant organic acids trapped within the calcite growth rings can be investigated using
3   luminescence studies and UV microscope technology. Fluorescence can be observed using
4   reflected light microscopy to detect emission wavelengths of between 400 and 480 nm with a
5   mercury light source to provide UV excitation at wavelengths of between 300 and 420 nm.
6   Trace element and UV-fluorescent laminae studies provide information at a finer resolution
7   (annual to subannual level) than the other techniques listed in Table 3, thereby offering the
8   potential to research the changing nature of seasonality through time. During periods of
9   higher or more intense precipitation, organic material can be washed on to the surface of
10   speleothems. By applying these techniques to investigate growth laminae, conclusions can
11   be drawn regarding the frequency of cyclonic storms and hence the changing atmospheric
12   circulation patterns (Baker et al., 1999; 2008; Soubiès et al., 2005).

13   Stable isotope studies of speleothems and tufas are now well established proxies for
14   interpreting climate change (Andrews, 2006; Baker et al., 2008; Andrews and Brasier, 2005;
15   McDermott, 2004, Richards et al., 1994). Garnett et al. (2006) carried out stable isotope
16   analyses of Late-glacial and early Holocene tufa deposits from Caerwys, North Wales, UK,
17   demonstrating that Late-glacial tufa (pre-9000 years BP) probably formed during a period of
18   climatic warming with summer water temperatures in the range 13 to 16.5°C, followed by a
19   period of cooling associated with the cessation of tufa precipitation. Analysis of oxygen
20   isotope ratios from pedogenic carbonates can also provide useful palaeoclimatic
21   information, reflecting changes in the humidity and frequency of soil wetting (Lowe and
22   Walker, 1997; Pendall et al., 1994).

1 Whilst laminar growth patterns have not been reported in secondary carbonate cements,
2 more than one type or phase of cement can be present and these can be used to interpret
3 depositional environments. For example, in a detailed petrological study carried out in
4 conjunction with stable isotope analyses, Strong et al. (1992) identified a range of cement
5 fabrics in carbonate cemented Late Devenesian glacial gravels.

6.3 Incision and the interpretation of groundwater base-levels

7   Speleothems have been used to determine sea level change, e.g. in the Bahamas (Gascoyne
8   et al., 1979 and Richards et al., 1994). Dating of secondary carbonate deposits also offers the
9   potential for determining rates of landscape incision. Where cemented rudites have formed
10 on a geomorphic or anthropogenic surface, dating of the cement provides a minimum age
11 for the host surface. This has been found to be particularly relevant to the dating of glacial
12 tills, e.g. Preece et al. (2007). In the situation that a dated surface has been incised, the
13 opportunity arises to calculate the rate of incision. It should be noted that the rate of incision
14 may equate to either surface lowering, or to glaciogenic or tectonic uplift. Calculations of
15 this type have been undertaken using dated tufa deposits in Lathkill Dale, Derbyshire, UK
16 (Banks et al., 2011).

17 Similarly, although it is feasible that more than one cave level can be hydraulically
18 operational at a given time, dating of speleothems has demonstrated that the oldest material
19 is commonly found in the higher caves and that the onset of speleothem formation is
20 progressively later in lower caves (Ford and Williams, 1989; Lowe and Walker, 1997). This
21 may be a response to the progressive lowering of the water table and therefore another
22 potential means of calculating rates of incision.

6.4 Carbon dioxide budgeting

24 The cycle of dissolution and precipitation of calcium carbonate involves carbon dioxide
25 cycling. Consequently, bacterial carbonate precipitation in terrestrial environments may be
26 crucial for atmospheric carbon dioxide budgeting (González-Muňoz et al., 2010).

6.5 Discriminating between point and diffuse contaminant sources

28 Monitoring the flux of dissolved species in streams in karst environments can provide
29 useful information regarding the functioning of karst aquifers, in particular to determine
30 sources and sinks of calcium carbonate. Associated with this, there is the potential to
31 discriminate between diffuse and point source contaminants in the stream environment.
32 Flow networks in karst aquifers facilitate the focusing of contaminants (Vesper et al., 2001).
33 The flux associated with the latter has a more discrete, spiky impact on water quality, which
34 is readily discernible with customised monitoring networks (Banks and Palumbo-Roe, 2010).

6.6 Dating of catastrophic events

36 Catastrophic events, such as earthquakes, can damage speleothems for which U-series dates
37 can be obtained (Forti, 1997; Ford and Hill, 1999). Equally, the occurrence of geohazard
38 events may be associated with secondary carbonate precipitation, e.g the Fern Pass
39 rockslide, Austria (Ostermann et al., 2007). This provided new sources of carbonate and new

1 flow paths, facilitating precipitation of secondary terrestrial carbonate deposits and
2 providing a means of dating such events in the geological record.

7. Conclusions

4 This overview of secondary terrestrial carbonate deposition in karst environments
5 demonstrates that the carbonates have a widespread distribution, display a variety of forms
6 and result from a range of depositional and diagenetic processes. Such variability has
7 resulted in numerous descriptive terms for the deposits as well as some complexities in
8 classification. Examples cited in this chapter illustrate how detailed studies of the
9 depositional setting, form and geochemistry of the carbonates can provide important
10 information about formative processes, age and past environmental conditions (climatic,
11 hydrogeological, hydrochemical, biological, geomorphological and anthropogenic). Such
12 studies have particular relevance to interpretations of climate change and landscape
13 evolution. Recent research has focused on the study of: terrestrial carbonate deposits in deep
14 time (Brasier, 2011); diagenetic processes (Brasier et al., 2011; Martín–Garcĺa et al., 2009);
15 refining dating techniques for tufas and carbonate cements (Sharp et al., 2003; Garnett et al.,
16 2004); dating using laser ablation linked ICPMS (Eggins et al., 2005); hyperspectral imaging
17 of secondary carbonate deposits (Jex et al., 2008); furthering understanding of depositional
18 processes, particularly the biological processes (Dittrick and Sibler, 2010; González-Muňoz
19 et al., 2010, and Jones, 2010); cave atmosphere and drip chemistry (Baldini et al., 2006);
20 collecting and interpreting continuous monitoring data (spring chemistry), and analysing
21 the reasons for tufa decline, e.g. eutrophication (Forbes et al., 2010). The ongoing description
22 and interpretation of "new" exposures of secondary carbonate deposits, e.g. Forbes et al.
23 (2010) has the potential to underpin the conceptual understanding of the hydrogeology of
24 these deposits.

8. Acknowledgements

9. Glossary

Activity constant:	The ratio of the apparent to the actual concentrations of ions that results from the inter-ionic forces of attraction in more concentrated solutions of a solute.
BP:	Before present.
Columnar:	Upright, elongate growth form.
Deamination:	Removal of an amine group (organic compound or functional group containing an N atom) from a molecule.
Dissociation constant:	Dissociation is a process whereby a single compound splits into two or more smaller products that can easily recombine to form the reactant. The dissociation constant reflects the extent of incomplete dissociation.

Doline: Enclosed depression centred on a sink hole, or intercepted cave passage.

Epikarst: Karst zone that lies closes to the surface, encompassing the soil and weathered bedrock.

EPS: Extracellular polymeric substances, which are characterised by the presence of different proteins, uronic acids, pyruvic acid and sulphate groups.

ICPMS: Inductively coupled plasma mass spectrometry.

Inception horizon: Part of a rock succession that is particularly susceptible to the earliest cave forming processes.

Luminescence: Light that usually occurs at low temperatures.

MC ICPMS: Multi collector inductively coupled plasma mass spectrometry.

Mucopolysaccharide: Polysaccharide containing an amino group.

Oncolite: Carbonate encrusted nodules developed around a stone, or another nucleus (Tucker, 2011; Viles and Goudie, 1990).

Palisade calcite: Calcite that is formed with elongate crystals perpendicular to the growth surface.

Picocyanobacteria: Microscopic (0.2-2.0 µm) bacteria.

Polysaccharide: Carbonate comprising a chain of sugars (monosaccharides) that be of more than one type.

Pyruvic acid: An organic acid and ketone ($CH_2COCOOH$).

Sheath: A bacterial sheath surrounds certain filamentous bacteria, particularly those in water.

Uronic acids: A sugar with carbonyl and carboxylic acid function.

Speleogenesis: Cave forming processes.

Stromatolites: A term that is used to describe cemented algal mats from the coastal zone and is commonly applied to freshwater deposits of a similar form (Tucker, 2011; Viles and Goudie, 1990).

TIMS: Thermal ionization mass spectrometry.

Twilight zone: Portion of the cave that forms the transition between the unlit cave interior and the outside world (Jones, 2010).

Vaterite: Metastable polymorph of calcium carbonate.

10. References

Aharon, P., Rasbury, M. and Murgulet, V. 2006. Caves of Niue Island, South Pacific: Speleothems and water geochemistry. In: Harmon, R.S. and Wicks, C. Editors. Perspectives on karst geomorphology, hydrology and geochemistry – A tribute volume to Derek C. Ford and William B. White: *Geological Society of America Special Paper,* 404, 283-295.

Andrews, J.E. 2006. Palaeoclimatic records from stable isotopes in riverine tufas: Synthesis and review. *Earth Science Reviews*, 75, 85-104.

Andrews, J.E., Pedley, H.M. and Dennis, P.F. 1994. Stable isotope record of palaeoclimatic change in a British Holocene tufa. *The Holocene,* 4, 349-355.

Andrews, J.E. and Brasier, A.T. 2005. Seasonal records of climatic change in annually laminated tufas: short review and future prospects. *Journal of Quaternary Science*, 20, 5, 411-421.

Appelo, C.A.J. and Postma, D. 2005. *Geochemistry, Groundwater and Pollution*. Balkema, Rotterdam. 536pp.

Atkinson, T.C. 1977a. Diffuse flow and conduit flow in limestone terrain in the Mendip Hills, Somerset (Great Britain). *Journal of Hydrology*, 35, 93-110.

Atkinson, T.C. 1977. Carbon dioxide in the atmosphere of the unsaturated zone: an important control of groundwater hardness in limestones. *Journal of Hydrology*, 35, 111-123.

Baker, A., Proctor, C.J., and Barnes, W.L. 1999. Variations in stalagmite luminescence laminae structure at Poole's Cavern, England, AD 1910-1996: calibration of a palaeoprecipitation proxy. *The Holocene*, 9, No. 6, 683-688.

Baker, A., Smith, C.L., Jex, C., Fairchild, I.J., Genty, D. and Fuller, L. 2008. Annually laminated speleothems: a Review. *International Journal of Speleology*, 37, 3, 193-206.

Baldini, J.U.L., McDermott, F. and Fairchild, I.J. 2006. Spatial variability in cave drip water hydrochemistry: Implications for stalagmite paleoclimate records. *Chemical Geology*, 235, 390-404.

Banks, V.J., Gunn, J. and Lowe, D.J. 2009. Stratigraphical influences on the limestone hydrogeology of the Wye catchment, Derbyshire. *Quarterly Journal of Engineering Geology and Hydrogeology*, 42, 211-225.

Banks, V.J. and Palumbo-Roe, B. 2010. Synoptic monitoring as an approach to discriminating between point and diffuse source contributions to zinc loads in mining impacted catchments. *Journal of Environmental Monitoring*, 12, 1684-1698.

Banks, V.J. Jones, P.F., Lowe, D.J., Lee, J.R., Rushton, J.C. and Ellis, M.A. 2011. Review of tufa deposition and palaeohydrological conditions in the White Peak, Derbyshire, UK: Implications for Quaternary landscape evolution. *Proceedings of the Geologists' Association* (in Press) 10.1016/j.pgeola.2011.03.011.

Bertenshaw, M. P. 1981. Hydrogeochemical indication of mineral deposits in the limestones of Derbyshire. *Transactions of the Institution of Mining and Metallurgy (Section : Applied Earth Science)*, 90, B167-B173.

Bischoff, J.L., Julia, R., Shanks, W.C. and Rosenbauer, R.J. 1994. Karstification without carbonic acid: Bedrock dissolution by gypsum-driven dedolomitization. *Geology*, 22, 995-998.

Brasier, A.T. 2011. Searching for travertines, calcretes and speleothems in deep time: Processes, appearances, predictions and the impact of plants. *Earth-Science Reviews*, 104, 213-239.

Brasier, A.T., Andrews, J.E. and Kendall, A.C. 2011. Diagenesis or dire genesis? The origin of columnar spar in tufa stromatolites of central Greece and the role of chironomid larvae. *Sedimentology, doi: 10.1111/j.1365-3091.2010.01208.x*.

Chafetz, H.S. and Folk, R.L. 1984. Travertines: depositional morphology and the bacterially constructed constituents. *Journal of Sedimentary Petrology*, 54, 289-316.

Chafetz, H.S., Utech, N.M. and Fitzmaurice, S.P. 1991. Differences in the $\delta^{18}O$ and $\delta^{13}C$ signatures of seasonal laminae comprising travertine stromatolite. *Journal of Sedimentary Geology*, 162, 199-218.

Chen, J., Zhang, D.D., Wang, S., Xiao, T. and Huang, R. 2004. Factors controlling tufa deposition in natural waters at waterfall sites. *Sedimentary Geology*, 166, 353-366.

Clarke, I and Fontes, J.C. 1990. Palaeoclimatic reconstruction in Northern Oman based on carbonates from hyperalkaline ground-waters. *Quaternary Research*, 33, 320-336.

Curtis, M.H. 2002. Pedogenic carbonate: links between biotic and abiotic CaCO₃. 17TH WCSS, 14-21 August, 2002, Thailand. Paper 897, 1-9.

Denniston, R.F., Gonzalez, L.A., Asmerom, Y., Sharma, R.H. and Reagan, M.K. 2000. Speleothem evidence for changes in Indian summer monsoon precipitation over the last 2300 years. *Quaternary Research,* 53, 196-202.

Dipova, N. 2011. The engineering properties of tufa in the Antalya area of SW Turkey. *Quarterly Journal of Engineering Geology and Hydrogeology,* 44, 123-134.

Dittrich, M. and Sibler, S. 2010. Calcium carbonate precipitation by cyanobacterial polysaccharides. In: Pedley,.M. and Rogerson, M. (Eds). 2010. *Tufas and Speleothems: Unravelling the Microbial and Physical Controls.* Geological Society, London, Special Publication, 336, 51-63.

Downing, R.A. 1967. *The geochemistry of groundwaters in the Carboniferous Limestone in Derbyshire and the East Midlands.* Bulletin No. 27. *Geological Survey of Great Britain*, 289-307.

Drake, J.J. and Harmon, R.S. 1973. Hydrochemical environments of carbonate terrains. *Water Resources Research*, 9, No. 4, 949-957.

Edmunds, W.M. 1971. *Hydrogeochemistry of groundwaters in the Derbyshire Dome with special reference to trace constituents.* IGS Report 71/7.

Edwards, R.l., Chen, J.H., Wasserburg, G.J. 1987. ^{238}U-^{234}U-^{230}Th-^{232}Th systematics and precise measurement of timeover the past 500, 000 years. *Earth and Planetary Science Letters* 81, 175-192.

Eggins, S.M., Grün, R., McCulloch, M.T. Pike, A.W.G., Chappell, J., Kinsley, L., Mortimer, G., Shelley, M., Murray-Wallace, C.V., Spötl, C. and Taylor, L. 2005. In situ U-series dating by laser-ablation multi-collector ICPMS: new prospects for Quaternary geochronology. *Quaternary Science Reviews*, 24, 2523-2538.

Faccenna, C., Soligo, M., Billi, A., De Filippis, L., Funiciello, R., Rossetti, C. and Tuccimei, P. 2008. Late Pleistocene depositional cycles of the Lapis Tiburtinus travertine (Tivoli, Central Italy): Possible influence of climate and fault activity. *Global and Planetary Change*, 63, 299-308.

Fairchild, I.J., Baker, A., Borsato, A., Frisia, S., Hinton, R.W., McDermott, F. and Tooth, A. 2001. Annual to sub-annual resolution of multiple trace-element trends in speleothems. *Journal of the Geological Society, London* 158, 831-841.

Fetter, C.W. 2001. *Applied Hydrogeology*. 4 th Ed. Prentice-Hall, Inc. 598 pp.

Forbes, M., Vogwill, R. and Onton, K. 2010. A characterisation of the coastal tufa deposits of south-west Western Australia. *Sedimentary Geology*, 232, 52-65.

Ford, D.C. and Williams, P.W. 1989. *Karst Geomorphology and Hydrology*. Unwin Hyman, London.

Ford, D.C. and Hill, C.A. 1999. Dating of speleothems in Kartchner Caverns, Arizona. *Journal of Cave and Karst Studies,* 6, 2, 84-88.

Ford, D.C. and Williams, P.W. 2007. *Karst Hydrogeology and Geomorphology*. John Wiley and Sons Limited. 562pp.

Ford, T.D. and Pedley, H.M. 1996. A review of tufa and travertine deposits of the world. *Earth Science Reviews*, 41, 117-175.

Forti, P. 1997. Speleothems and Earthquakes. In Hill, C. and Forti, P.(Editors) *Caves and minerals of the world.* National Speleological Society, Huntsville, 284-285.

Francis, J.E. 1984. The seasonal environment of the Purbeck (upper Jurassic) fossil forests. *Palaeogeography, Paleoclimatology, Palaeoecology,* 48, 2-4, 285-307.

Fuller, L., Baker, A., Fairchild, I.J., Spötl, C., Marca-Bell, A., Rowe, P. and Dennis, P.F. 2008. Isotope hydrology of dripwaters in a Scottish cave and implications for stalagmite palaeoclimate research. *Hydrology and Earth System Sciences Discussions*, 5, 547-577.

Garnett, E.R., Gilmour, M.A., Rowe, P.J., Andrews, J.E. and Preece, R.C. 2004. ^{230}Th/^{234}U dating of Holocene tufas: possibilities and problems. *Quaternary Science Reviews,* 23, 947-959.

Garnett, E.R., Andrews, J.E., Preece, R.C. and Dennis, P.F. 2006. Late-glacial and early Holocene climate and environment from stable isotopes in Welsh tufa. *Quaternaire*, 17 (2), 31-42.

Gascoyne, M., Benjamin, G.J. Schwarcz, H.P. and Ford, D.C. 1979. Sea level lowering during the Illinoian glaciation: evidence from a Bahama "blue hole". *Science*, 205, 806-808.

Genty, D. and Quinif, Y. 1996. Annually laminated sequences in the internal structure of some Belgian stalagmites-importance for palaeoclimatology. *Journal of Sedimentary Research,* 66, No. 1, 275-288.

Glover, C. and Robertson, A.H.F. 2003. Origin of tufa (cool-water carbonate) and related terraces in the Antalya area, SW Turkey. *Geological Journal,* 38, 329-358.

González-Muňoz, M.T., Rodriguez-Navarro, C., Martīnez-Ruiz, F., Arias, J.M, Merroun, M.L. and Rodriguez-Gallego, M. 2010. Bacterial biomineralization: new insights from Myxococcus-induced mineral precipitation. In: Pedley, .M. and Rogerson, M. (Eds). 2010. *Tufas and Speleothems: Unravelling the Microbial and Physical Controls*. Geological Society, London, Special Publication, 336, 31-50.

Goudie, A.S., Viles, H.A. and Pentecost, A. 1993. The late-Holocene tufa decline in Europe. *The Holocene*, 3, 181-186.

Grün, R. 1989. Electron spin resonance (ESR) dating. *Quaternary International,* 1, 65-109.

Gunn, J. 1981. Limestone solution rates and processes in the Witomo district, New Zealand. *Earth Surface Processes and Landforms*, 6, 427-45.

Gunn, J. 1986. Solute processes and karst landforms. In *Solute Processes.* Ed. Trudgill, S.T. John Wiley and Sons Ltd. pp. 363-437.

Han, G. and Liu, C-G. 2004. Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China. *Chemical Geology*, 204, 1-21.

Hill, C.A. and Forti, P. 1995. The classification of cave minerals and speleothems. *International Journal of Speleogenesis* 24, 1-4, 77-82.

Immenhauser, A., Buhl, D., Richter, D., Niedermayr, A., Riechelmann, D., Dietzel, M. and Schulte, U. 2010. Magnesium-isotope fractionation during low-Mg calcite precipitation in a limestone cave-Field study and experiments. *Geochimica et Cosmochimicia Acta*, 74, 4346-4364.

Jacobson, R.L. and Langmuir, D. 1974. Controls on the quality variations of some carbonate spring waters. *Journal of Hydrology*, 23, 247-265.

Jex, C., Claridge, E, Baker, A. and Smith, C. 2008. Hyperspectral imaging of speleothems. *Quaternary International*, 187, 5-14.

Jones, B. 2010. Microbes in caves: agents of calcite corrosion and precipitation. In: Pedley,.M. and Rogerson, M. (Eds). 2010. *Tufas and Speleothems: Unravelling the Microbial and Physical Controls*. Geological Society, London, Special Publication, 336, 7-30.

1   Kaufmann, G. and Dreybrodt, W. 2007. Calcite dissolution kinetics in the system $CaCO_3$-
2   H_2O-CO_2 at high undersaturation. *Geochimica et Cosmochimica Acta*, 71, 1398-1410.
3   Kawai, T, Kano, a., Matsuoka, J., and Ihara, T. 2006. Seasonal variation in water chemistry
4   and depositional processes in a tufa-bearing stream in SW-Japan, based on 5 years
5   of monthly observations. *Chemical Geology*, 232, 33-53.
6   Kendall, A.C. and Broughton, P.L. 1978. Origin of fabrics in speleothems composed of
7   columnar calcite crystals. *Journal of Sedimentary Research*, 48, 2, 519-538.
8   Kehew, A.E. 2001. Applied chemical hydrogeology. Prentice Hall. 368 pp.
9   Lauritzen, S.E. 1993. Natural environmental change in karst: the Quaternary record. In
10   Williams, P.W. (Editor) Karst Terrains: Environmental Changes and Human
11   Impact. *Catena Supplement,* 25, Catena Verlag, Cremlingen-Destedt, Germany, 21-
12   40.
13 Leybourne, M.I., Betcher, R.N., McRitchie, W.D., Kaszycki, C.A. and Boyle, D.R. 2009.
14   Geochemistry and stable isotopic composition of tufa waters and precipitates from
15   the Interlake Region, Manitoba, Canada: Constraints on groundwater origin,
16   calcitization, and tufa formation. *Chemical Geology*, 260, 3-4, 221-233.
17 Liu, Z., Li, Q., Sun, H. and Wang, J. 2007. Seasonal, diurnal and storm-scale hydrochemical
18   variations of typical epikarst springs in subtropical karst areas of SW China: Soil
19   CO_2 and dilution effects. *Journal of Hydrology*, 337, 207-223.
20 Lorah, M.M. and Herman, J.S. 1988. Chemical evolution of a Travertine Depositing Stream.
21   *Water Resources Research*, 24, No.9, 1541-155.
22 Love, K.M. and Chafetz, H.S. 1988. Diagenesis of laminated travertine crusts, Arbuckle
23   Mountains, Oklahoma. *Journal of Sedimentary Research*, 58, 441-445.
24 Lowe, D.J. 2000. Role of stratigraphic elements in speleogenesis: the speleoinception
25   concept. In: *Speleogenesis evolution of karst aquifers.* Eds. Klimchouk, A.B., Ford,
26   D.C., Palmer, A.N. and Dreybrodt, W. pp. 65-76.
27 Lowe, J.J. and Walker, M.J.C. 1997. Reconstructing Quaternary Environments. Second
28   Edition. Pearson Prentice Hall 446 pp.
29 Manning, D.A.C. 2008. Biological enhancement of carbonate precipitation: passive removal
30   of atmospheric CO_2. *Mineralogical Magazine*, 72 (2), 639-649.
31 MartÍn-GarcÍa, R., Alonso-Zarza, A.M. and MartÍn-Pérez, A. 2009. Loss of primary texture
32   and geochemical signatures in speleothems due to diagenesis: Evidences from
33   Castaňar Cave, Spain. *Sedimentary Geology*, 221, 141-149.
34 Matsuoka, J., Kano, A., Oba, T., Watanabe, T., Sakaǐ, S. and Seto, K. 2001. Seasonal variation
35   of stable isotopic compositions recorded in laminated tufa, SW Japan. *Earth and
36   Planetary Science Letters,* 192, 31-44.
37 McDermott, F. 2004. Paleo-climate reconstruction from stable isotope variations in
38   speleothems: a review. *Quaternary Science Reviews,* 23, 901-918.
39 McGarry, S.F. and Caseldine, C. 2004. Speleothem palynology: an undervalued tool in
40   Quaternary studies. *Quaternary Science Reviews,* 23, 2389-2404.
41 Ostermann, M., Sanders, D., Prager, C. and Kramers, J. 2007. Aragonite and calcite
42   cementation in "boulder controlled" meteoric environments on the Fern Pass
43   rockslide (Austria): implications for radiometric age dating of catastrophic mass
44   movements. *Facies*, 53, 189-208.
45 Palmer, A.N. 1991. Origin and morphology of caves. *Geological Society of America Bulletin,*
46   103, 1-21.

1 Palmer, A.N. 2002. Speleogenesis in carbonate rocks. In: *Evolution of Karst: From Prekarst to*
2   *Cessation.* Gabrovsek, F.(Editor). Postojna. pp. 43-59.
3 Pazdur, A., Pazdur, M.F. and Szulc, J. 1988. Radiocarbon dating of Holocene calcareous tufa
4   in Southern Poland. *Radiocarbon,* 30, 133-151.
5 Pedley, H.M. 1990. Classification and environmental models of cool freshwater tufas.
6   *Sedimentary Geology,* 68, 143-154.
7 Pedley, M.H. and Rogerson, M. 2010. Introduction to tufas and speleothems. In: Pedley, .M.
8   and Rogerson, M. (Eds). 2010. *Tufas and Speleothems: Unravelling the Microbial and*
9   *Physical Controls.* Geological Society, London, Special Publication, 336, 1-5.
10 Pendall, E.G., Harden, J.W., Trumore, S.E. and Chadwick, O.A. 1994. Isotopic approach to
11   soil carbonate dynamics and palaeoclimatic interpretations. *Quaternary Research,* 42,
12   60-71.
13 Pentecost, A. 1978. Blue-green algae and freshwater carbonate deposits. *Proceedings of the*
14   *Royal Society of London B* 200, 43-61.
15 Pentecost, A. 1988. Growth and calcification of the Cyanobacterium *Homoeothrix crustacea.*
16   *Journal of General Microbiology*, 134, 2665-2671.
17 Pentecost, A. 1991. Calcification processes in algae and cyanobacteria. In: Riding, R. (ed)
18   Calcareous *Algae and Stromatolites*. Springer, Berlin, 3-20.
19 Pentecost, A. 1995. The Quaternary travertine deposits of Europe and Asia Minor.
20   *Quaternary Science Reviews*, 14, 1005-1028.
21 Pentecost, A. 1999. The origin and development of the travertines and associated thermal
22   waters at Matlock Bath, Derbyshire. *Proceedings of the Geologists' Association,* 110,
23   217-232.
24 Pentecost, A. and Lord, T. 1988. Postglacial tufas and travertines from the Craven district of
25   Yorkshire. *Cave Science* 15, 15-19.
26 Pentecost, A. and Viles, H.A. 1994. A review and reassessment of travertine classification.
27   *Géographie physique et Quaternaire*, 48, 3, 305-314.
28 Pitty, A.F. 1966. *An Approach to the Study of Karst Water*, 59 (University of Hull Occasional
29   Papers in Geography, 5).
30 Pitty, A.F. 1968. The scale and significance of solutional loss from the limestone tract of
31   southern Pennines. *Proceedings of the Geologists' Association*, 79 (2), 153-177.
32 Preece, R.C., Parfitt, S.A., Bridgland, D.R., Lewis, S.G., Rowe, P.J., Atkinson, T.C., Candy, I.,
33   Debenham, N.C., Penkman, K.E.H., Rhodes, E.J., Schwenninger, J-L., Griffiths, H.I.,
34   Whittaker, J.E. and Gleed-Owen, C. 2007. Terrestrial environments during MIS 11:
35   evidence from the Palaeolithic site at West Stow, Suffolk, UK. *Quaternary Science*
36   *Reviews*, 26, 1236-1300.
37 Railsback, L.B., Brook, G.A., Chen, J. 1994. Environmental controls on the petrology of a late
38   Holocene speleothem from Botswana with annual layers of aragonite and calcite.
39   *Journal of Sedimentary Research*, 64, 147-155.
40 Richards, D.A. and Dorale, J.A. 2003. Uranium-series Chronology and Environmental
41   Applications of Speleothems. In: *Uranium-series Geochemistry* (Editors B Bourdon,
42   G.M. Henderson, C.C. Lundstrom and S.P. Turner). *Reviews in Mineralogy and*
43   *Geochemistry,* 52, 407-461.
44 Richards, D.A., Smart, P.L. and Lawrence Edwards, R. 1994. Maximum sea levels for the last
45   glacial period from U-series ages of submerged speleothems. *Nature,* 367, 357-360.

Richardson, T.D. 1968. The use of chemical analysis of cave waters as a method of water tracing and indicator of type of strata traversed. *Transactions of the Cave Research Group of Great Britain,* 10, 2, 61-72.

Riding, R. 2000. Microbial carbonates: the geological record of calcified bacterial-algal mats and biofilms. *Sedimentology Supplement 1*, 47, 179-214.

Rieuwerts, J.H. 2000. *Lathkill Dale Derbyshire its Mines and Miners*. Landmark Publishing Limited. 110pp.

Rowe, P., Austin, T., and Atkinson, T. 1988. The Quaternary evolution of the British South Pennines from Uranium series and Palaeomagnetic data. *Annales de la Société géologique de Belgique*, T. 111, 97-106.

Selim, H.H. and Yanik, G. 2009. Development of the Cambazh (Turgutlu/MANISA) fissure-ridge-type travertine and relationship with active tectonics, Gediz Graben, Turkey. *Quaternary International,* 199, 157-163.

Sharp, W.D. Ludwig, K.R., Chadwick, O.A., Admundson, R. and Glaser, L.L. 2003. Dating fluvial terraces by ^{230}Th/U on pedogenic carbonate, Wind River Basin, Wyoming. *Quaternary Research*, 59, 139-150.

Sherwin, C.M. and Baldini, J.U.L. 2011. Cave air and hydrological controls on prior calcite precipitation and stalagmite growth rates: Implications for palaeoclimate reconstructions using speleothems. *Geochimica et Cosmochimica Acta*, 75, 3915-3929.

Shuster, E. T. and White, W. B. 1971. Seasonal fluctuations in the chemistry of limestone springs: a possible means for characterizing carbonate aquifers. *Journal of Hydrology*, 14, 93-128.

Şimşek, S. 1993. Karstic hot water aquifers in Turkey. In Hydrogeological Processes in Karst Terranes (Proceedings of the Antalya Symposium and Field Seminar, October, 1990; IAHS Publication 207).

Smith, D.I. and Atkinson, T.C. 1976. Process, landforms and climate in limestone regions, 367-409. In: Derbyshire, E. Ed. *Geomorphology and Climate*, 512pp.

Soubiès, F., Seidel, A., Mangin, A., Genty, D., Ronchail, J., Plagnes, V., Hirooka, S. and Santos, R. 2005. A fifty-year climatic signal in three Holocene stalagmite records from Mato Grosso, Brazil. *Quaternary International,* 135, 115-129.

Strong, G.E., Giles, J.R.A. and Wright, V.P. 1992. A Holocene calcrete from North Yorkshire, England: implications for interpreting palaeoclimates using calcretes. *Sedimentology*, 39, 333-347.

Sweeting, M.M. 1966. The weathering of limestones, with particular reference to the Carboniferous Limestones of northern England. In: Dury, G.H. (Editor) *Essays in Geomorphology*. Heinemann. London. pp. 177-210.

Taylor, D.M., Griffiths, H.I., Pedley, H.M. and Prince, I. 1994. Radiocarbon-dated Holocene pollen and ostracod sequences from barrage tufa-dammed fluvial systems in the White Peak, Derbyshire, U.K. *The Holocene*, 4, No.4, 356-364.

Terjesen, S.G., Egra, O., Thoresen, G. and Ve, A. 1961. Phase boundary processes as rate determining steps in reactions between solids and liquids. The inhibitory action of metal ions on the formation of calcium bicarbonate by the reaction of calcite with aqueous carbon dioxide. *Chemical Engineering Science*, 14, 277-289.

Thrailkill, J. 1968. Chemical and Hydrologic Factors in the Excavation of Limestone Caves. *Geological Society of America Bulletin*, 79, 19-46.

Tooth, A.F. and Fairchild, I.J. 2003. Soil and karst aquifer hydrological controls on the geochemical evolution of speleothem-forming drip waters, Crag Cave, southwest Ireland. *Journal of Hydrology,* 273, 51-68.

Tucker, M.E. 2011. *Sedimentary rocks in the Field: a practical guide*. Wiley Blackwell. 275 pp.

Tucker, M.E. and Wright, P.V. 1990. Carbonate Sedimentology. Blackwell Science Ltd. 482pp.

Vervier, P. 1990. Hydrochemical characterization of the water dynamics of a karstic system. *Journal of Hydrology*, 121, 103-117.

Vesper, D.J., Loop, C.M. and White, W.B. 2001. *Contaminant transport in karst aquifers. Theoretical and Applied Karstology*, 13-14, 101-111.

Viles, H.A. and Goudie, A.S. 1990. Tufas, travertines and allied carbonate deposits. *Progress in Physical Geography*, 14, 19-41.

Viles, H.A. and Pentecost, A. Tufa and Travertine. In: Nash, D.J. and McLaren, S.J. (Editors) 2007. Geochemical sediments and landscapes. Blackwell Publishing. pp. 173-199.

White, W.B. 2002. Karst hydrology: recent developments and open questions. *Engineering Geology*, 65, 85-105.

Woo, K.S. and Choi, D.W. 2006. Calcitization of aragonite speleothems in limestone caves in Korea: Diagenetic process in a semiclosed system. In: Harmon, R.S. and Wicks, C. Editors. Perspectives on karst geomorphology, hydrology and geochemistry – A tribute volume to Derek C. Ford and William B. White: *Geological Society of America Special Paper,* 404, 297-306.

Worthington, S.R.H. 1991. *Karst Hydrogeology of the Canadian Rocky Mountains*. Unpublished Ph.D. thesis. McMaster University. 370pp.

Worthington, S.R.H. and Ford, D.C. 1995. High Sulfate concentrations in limestone springs: An important factor in conduit initiation? *Environmental Geology*, 25, 9-15.

Zhou, J. and Chafetz, H.S. 2010. Pedogenic Carbonates in Texas: Stable-Isotope Distributions and Their Implications for Reconstructing Region-Wide Paleoenvironments. *Journal of Sedimentary Research*, 80, 2, 137-150.