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Linking process and product in terrestrial carbonates using a solution thermodynamic approach

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Abstract

Determining the processes which generate terrestrial carbonate deposits (tufas, travertines and associated chemical sediments) is a long-standing problem. Deposition of mineral products from solution reflects a complex combination of biological, equilibrium and kinetic processes, and the differences in products these processes produce are yet to be clearly demarked. Building on the groundbreaking work of previous authors, we propose that the underlying control on the processes leading to the deposition of these products can be most parsimoniously understood from the thermodynamic properties of their source solutions. Here, we report initial observations of the differences in product generated from spring and lake systems spanning a range of temperature: supersaturation space. We find that at high supersaturation, biological influences are masked by high rates of spontaneous nucleation and sedimentary products from these settings infrequently exhibit classic “biomediated” fabrics such as clotted micrite. Likewise, at high temperature exclusion of vascular plants and complex/diverse biofilms significantly inhibits the magnitude of biomediated precipitation, again impeding the likelihood of encountering the “bio-type” fabrics.

Conversely, despite the clear division in product between extensive tufa facies associations and discontinuous deposits such as oncoid beds, no clear division can be identified between these systems in temperature: supersaturation space. We reiterate the conclusion of previous authors, which demonstrate that this division cannot be made on the basis of physico-chemical characteristics of the solution alone. We further provide a new case study of this division from two adjacent systems in the UK, where continuous tufa-like deposition is happening at a site with lower supersaturation than other sites exhibiting only discontinuous (oncoidal) deposition. However, a strong microbiological division is demonstrated between these sites on the basis of suspended bacterial cell distribution, which reach a prominent maximum where tufa-like deposits are forming.

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We conclude that at high supersaturation, the thermodynamic properties of solutions provide a highly satisfactory means of linking process and product, raising the opportunity of identifying water characteristics from sedimentological/petrological characteristics of ancient deposits. At low supersaturation, we recommend that future research focuses on geomicrobiological processes rather than the more traditional, inorganic solution chemistry approach dominant in the past.

1 Introduction

Terrestrial carbonate deposits have outstanding potential to act as an archive of climatic change (Andrews, 2006) and/or changes in the behaviour of crustal fluids (Minissale, 2004). However, despite their high potential and the considerable research effort that has already been expended on them there remains considerable debate and confusion over how mineral-forming processes can be linked to the sedimentology and petrology of tufas, travertines and other terrestrial chemical deposits. Early efforts were based on straightforward applications of conventional carbonate petrographic schemes. The standard scheme of Dunham (1962) modified by Embury and Kloven (1972) works admirably for most freshwater limestones, but lacks precision on account of the numerous biological elements present and makes no attempt to link product to process. Considerable advances from these early efforts have been made for geothermal deposits by numerous authors (Chafetz and Folk, 1984; Folk and Chafetz, 1983; Carrara et al., 1998; Carrara, 1994; Folk, 1994; Folk et al., 1985) and this has been further developed by Guo and Riding (1998). Much of the current petrographic terminology applied to ambient temperature tufas has also developed upon the Folk and Dunham schemes (see Pentecost, 2005). However, to date no single petrographic scheme has proven sufficiently effective to become standard.

In contrast, a diverse group of field classification schemes have independently been developed specifically for freshwater carbonates (Stirn, 1964; Irion and Müller, 1968; Schneider et al., 1983; Pentecost and Lord, 1988) emphasising; the role of botanical

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elements (Pentecost and Lord, 1988); their distinct geomorphological expression within the landscape (Symoens et al., 1951; Golubić, 1969; Nicod, 1981; Szulc, 1983); or combinations of biological and geomorphological aspects (Buccino et al., 1978; Ferreri, 1985; D'Argenio and Ferreri, 1988; Golubić et al., 1993). Others (e.g. Julia, 1983; Golubić, 1969) have discussed a process-based approach frequently involving cyclic progression of the facies, and an important observation to arise from more recent classifications was the role played by the phytoherm (freshwater reef) in tufa accumulation (see discussion in Pedley, 1992, 1990). This work was drawn together by Pedley (1990) and Ford and Pedley (1997) who offered an integrated, rationalised scheme for classifying freshwater carbonates which embraced both laboratory and field scales. Modifications of these schemes are now available for tropical tufas (e.g. Carthew et al., 2006) and new controls on individual facies arise on continuing field (Drysdale et al., 2003b; Brasier et al., 2011) and laboratory-based research (Pedley and Rogerson, 2010a). Alternative field classifications continue to evolve (e.g. Glover and Robertson, 2003; Peña et al., 2000, for tufas), but these schemes are yet to be updated to reflect recent developments in understanding biofilm processes (Decho, 2010).

Moreover, there remains a lack of a single scheme that adequately discriminates both geothermal and meteoric-type deposits simultaneously. Attempts have also been made to bridge and update existing classification schemes to also encompass geothermal deposits (e.g. Jones and Renaut, 2010), but these remain focussed on products at the expense of knowledge about processes. In this regard, it is surprising that there has not yet been an attempt to classify these deposits on the basis of whether they are dominantly biomediated or physico-chemical deposits. In the light of new insights into these processes arising from experimental work (Pedley and Rogerson, 2010b; Pedley et al., 2009; Bissett et al., 2008a; Shiraishi et al., 2008b), this is a major shortcoming.

Ultimately, we are yet to achieve the goal of a universally effective classification for terrestrial deposits that adequately reflect their unique modes of origin. Understanding how processes can be read from products is a key step on that journey.

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Major stumbling blocks remain to achieving the key step of aligning process and product in these systems into a single systematic view. Most seriously, the independent development of terminology between ambient temperature deposits and thermal deposits maintains the division of these communities. Even the basic terminology distinguishing terrestrial carbonates is not without conflict as some workers (e.g. Pentecost, 2005; Pentecost and Viles, 1994) recommend that all freshwater deposits should be called travertines, with the caveat that the prefixes “meteogene” or “thermogene” be applied for deposits in which the original precipitating source waters are either cool, shallow circulation-meteoric or hot, deep circulation (thermogene, with temperatures typically 20–60 degrees centigrade at the point of emergence). Others (including the authors of this manuscript) recommend that travertine is reserved only for deposits in geothermal settings. The pressing need to see all terrestrial carbonate systems as related and not independent of each other is emphasised by the case of *all* “thermogene” or “travertine” systems, where vegetation colonisation occurs as waters cool towards ambient temperatures, resulting in deposits which are often indistinguishable from “meteogene” “tufas”. While we argue that there is an advantage in retaining the terms “tufa” and “travertine” to distinguish *the source of the ions* precipitating from the system, we simultaneously recognise that the downside of a simple division in terms of temperature is that alkaline lakes (e.g. Mono Lake, Connell and Dreiss, 1995) may generate deposits significantly different to normal “tufa” regardless of being ambient in terms of temperature.

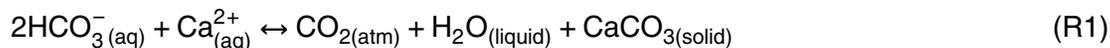
Here we attempt the first steps to overcome these stumbling blocks, building on the huge progress made in understanding the relationships between various types of deposits by previous workers outlined above, and propose a new direction in summarising precipitating system solution chemistry using simple thermodynamic concepts. Our thermodynamic approach is based on the assumption that physico-chemical forcing of precipitation will ultimately be a product of high Gibbs free energy in the solution the precipitation is derived from, as first proposed by Dandurand et al. (1982).

1.1 Carbonate precipitation mechanisms in terrestrial, open-water settings

1.1.1 Hydrochemical controls

To drive rapid precipitation, high levels of excess dissolved calcium carbonate are necessary in the ambient water. Consequently, the primary partition between tufa-forming and non-tufa river systems should coincide with some threshold in calcite supersaturation. However, Pentecost (1992) showed that in the Yorkshire Dales (UK) no systematic relationship between precipitation and degree of calcium carbonate supersaturation was present. An additional problem of this view is that the activation energy for calcite is $-48.1 \text{ kJ mol}^{-1}$ (Inskeep and Bloom, 1985) whereas the onset of significant riverine calcium carbonate deposition is considerably lower (e.g. -7 kJ mol^{-1} , Dandurand et al., 1982) leaving a wide energetic gap between where spontaneous nucleation would be expected to form from thermodynamic principals and where precipitation is found in natural systems. It is therefore already abundantly clear that thermodynamic considerations are not sufficient to explain site-to-site differences at low supersaturation, that kinetic and “surface” conditions are responsible for managing the thermodynamic barrier to precipitation and other explanation of these additional conditions must be sought.

At higher supersaturation, physico-chemical precipitation (i.e. that regulated by classic thermodynamic considerations) occurs either due to ingassing of atmospheric $\text{CO}_{2(\text{g})}$ under hyperalkaline conditions due to the presence of excess $\text{OH}^{-}_{(\text{aq})}$ (Clark and Fontes, 1990; Andrews et al., 1997) or, more normally, due to outgassing of CO_2 to atmosphere due to the presence of excess $\text{HCO}_3^{-}_{(\text{aq})}$ (Emeis et al., 1987). Rapid loss of $\text{CO}_{2(\text{aq})}$ primarily occurs when fresh spring waters come into contact with air depleted in CO_2 relative to aquifer air (Chafetz and Folk, 1984). Degassing-driven precipitation occurs according to the le Chatellier principle via;



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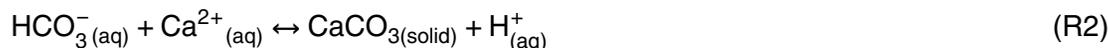
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rather than its impact on calcite saturation that is critical to initiating nucleation (Dandurand et al., 1982). If kinetics are dominant, different reaches and even different layers of water at a single reach of a freshwater systems may have very different saturation characteristics. Surface layer kinetic influences will ultimately be bound up with water flow structure, which regulate vertical ion transport rates. These authors are not aware of any specific study of flow structure in these settings. Bottom layer kinetic influences are fully understood, however.

1.1.2 Bottom layer kinetic influences; the diffusive boundary layer

At sites with flowing water, flow separation occurs at the water-carbonate interface, forming a boundary layer across which ions are exchanged primarily by diffusion (Zaihua et al., 1995; Liu and Dreybrodt, 1997; Dreybrodt and Buhmann, 1991). Consequently, precipitation-inhibiting H^+ ions tend to accumulate at the water-carbonate interface via precipitation originating from bicarbonate;



This drives down pH, causing conversion of $CO_3^{2-}_{(aq)}$ to $HCO_3^-_{(aq)}$ and reducing saturation. Investigation of tufa depositing rivers in China (Zaihua et al., 1995) showed that the consequence of this behaviour was that deposition rates in fast flowing water are higher than still water by a factor of four. This mechanism has also been investigated via numerical modelling, which suggests that it may be a fundamental control on the patterns of development of tufa barrages (Hammer et al., 2007, 2008; Hammer, 2008; Veysey and Goldenfeld, 2008). Indeed, a degree of consensus is emerging from this work that “equilibrium” degassing at sites of enhanced flow has very little impact on the rate of precipitation, which is essentially driven by enhanced vertical ion flux, particularly where flows become unstable (Hammer et al., 2010). This consensus in the physical literature is yet to be fully recognised in the sedimentological literature.

1.2 Biological factors

The mechanisms and state of knowledge of microbially induced and influenced calcite precipitation has recently been thoroughly reviewed (Dupraz et al., 2009). Consequently, we here aim to only summarise the most relevant parts of the very extensive knowledge concerning microbe-calcite interaction.

1.2.1 Photosynthesis and respiration

Consumption of CO_2 by photosynthesis results in enhanced pH, and consequently in increased proportion of dissolved inorganic carbon present as $\text{CO}_3^{2-}(\text{aq})$, close to the bodies of micro- and macrophytes as well as phototrophic microbes such as cyanobacteria. Consequently, when photosynthesis occurs in solutions at or near saturation with respect to CaCO_3 , calcite may precipitate as sheaths around algal filaments and coatings on plants (Pentecost, 1978, 1987). Respiration operates in the inverse sense, tending to increase dissolved CO_2 levels, reduce pH and inhibit precipitation. Consequently, tufa systems exist within a dynamic equilibrium where precipitation may be triggered or prevented by the balance of microbial metabolic processes (Visscher and Stolz, 2005; Decho, 2010). This balance will primarily reflect the state of health of the biofilm itself, as a growing community must, by definition, be consuming more carbon than it is releasing and vice versa. The impact of microbial metabolisms is well reflected in an investigation of chemical fluxes associated with calcite precipitating solutions, which indicates increased flux of Ca^{2+} and HCO_3^- to biofilm-encrusted surfaces relative to non-encrusted surfaces in high light conditions, but the reverse under dark conditions (Shiraishi et al., 2008a). Curiously, biofilms are capable of modifying their microenvironment so that the pH of interstitial water remains constant regardless of changes in the macroenvironment (Bissett et al., 2008b), so this effect may actually be amplified under low ambient pH conditions. Certainly, influxes of low pH water, argued by Pentecost (1992) to be a potential explanation for the absence of tufa from certain stream in Yorkshire, would have to be rather persistent to alter the ability of biofilms to

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synthesis of these enzymes are partly responsible for the ability of biofilm to regulate their internal pH (Bissett et al., 2008b), and they are therefore material to understanding why the lower limit of thermodynamic precipitation of calcite is so difficult to define (see Sect. 1.1.1).

5 1.2.4 Biofilms as bioreactors

In addition to providing a concentrated zone of photosynthesis, an abundance of nucleation sites and effective buffering of changes in external pH, they also provide a substrate in which bacteria with anaerobic metabolisms may flourish (Shiraishi et al., 2008c; Visscher and Stolz, 2005). These biofilm ecologies combine to create an “alkalinity engine” the regulation, operation and impact of which are only partially understood (Dupraz et al., 2009). In solutions buffered by bicarbonate, anaerobic metabolisms will either promote or impede precipitation, depending on the specific stoichiometry of the electron donation-absorption system (Visscher and Stolz, 2005), as summarised in Table 1. Given the range of chemistries possible in alkaline spring systems, all of these components of the alkalinity engine are possibly occurring within the sites we are interested in. However, the most likely anaerobic metabolism found in these systems is sulphate reduction. As this metabolism promotes generation of alkalinity, it can be assumed that non-aerobic degradation of organic matter favours mineralisation of calcite.

2 Methods and source of case study data

20 If we are to discriminate systems on the basis of whether biologically induced/influenced calcite precipitation is significant, and whether this precipitation is related to simple (exclusively microbial) or more complex ecologies (involving macrophytes) we first need to assess the magnitude of the chemical force promoting spontaneous nucleation of calcite.

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The Gibbs free energy of an ion pair in solution (e.g. $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{CO}_{3(\text{aq})}^{2-}$) can be straightforwardly estimated from its state of saturation (Dandurand et al., 1982) via:

$$\Omega G = -RT \quad (1)$$

where G is the Gibbs Free Energy of the solution (in kJ), R is the ideal gas constant ($8.314472 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$), T is the temperature (in Kelvin) and Ω is the saturation index with respect to the ion pair of interest.

Saturation of a carbonate solution is generally calculated using a chemical model, such as PHREEQC. However, these models are generally developed for freshwater systems, and the high ionic strength of some travertine-depositing systems (which can be higher than seawater, Tiziano, 2011) complicates their use across the entire range of terrestrial carbonates. The use of different models, or indeed different generations of the same model, may also cause differences in derived parameters such as G . Moreover, different published works present different quantities of data regarding minor ions, making an approach based on model-based convergence of the solution charge balance partially dependent on the nature of the source. To circumvent these potential issues, here we estimate Ω values analytically. A further advantage of using this approach is that it makes the internal calculations underlying our approach explicit to any reader.

The fundamental relationship underlying our analytical approach is

$$\Omega = \ln \frac{\gamma_1 [\text{Ca}_{(\text{aq})}^{2+}] \gamma_2 [\text{CO}_{3(\text{aq})}^{2-}]}{k_{\text{sp}}} \quad (2)$$

where γ_1 and γ_2 are the activity coefficients for $\text{Ca}_{(\text{aq})}^{2+}$ and $\text{CO}_{3(\text{aq})}^{2-}$ respectively, squared brackets indicate concentrations (in moles) and k_{sp} is the saturation coefficient of calcite, which is dependent on temperature and calculated from (Plummer and Busenberg, 1982)

$$k_{\text{sp}} = 10^{\{-171.9065 - (0.077993T) + (\frac{2839.31}{T}) + (71.595(\log_{10} T))\}} \quad (3)$$

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Activity coefficients γ_1 and γ_2 are calculated according to (Robinson and Stokes, 2002)

$$\log_{10} \gamma_1 = (-4\alpha l^{0.5}) / (1 + \beta A_{\text{Ca}} l^{0.5}) \quad (4)$$

$$\log_{10} \gamma_2 = (-4\alpha l^{0.5}) / (1 + \beta A_{\text{CO}_3} l^{0.5}) \quad (5)$$

5 where l is the ionic strength of the solution, A_{Ca} and A_{CO_3} are the bond lengths of these ions in calcite (1.14×10^{-10} and 1.36×10^{-10} Angstroms, respectively) and α and β are coefficients calculated from

$$\alpha = \left\{ \frac{(q_0^2 N_A)}{((2.303RT)(8\pi\epsilon_0\epsilon_T))} \right\} \beta \quad (6)$$

and

$$10 \quad \beta = \left\{ \frac{2000 N_A^2 q_0^2}{(\epsilon_0 \epsilon_T RT)} \right\}^{0.5} \quad (7)$$

where q_0 is an electron volt (1.6021×10^{-19} J), N_A is Avogadro's number (6.023×10^{23}), ϵ_0 is the permittivity of free space (8.8542×10^{-12} C² N⁻¹ m⁻²) and ϵ_T reflects thermal expansion and can be calculated from

$$\epsilon_T = 249.21 + 0.79069T + 0.72997 \times 10^{-3}T^2 \quad (8)$$

15 An additional complication of using existing field data is that the typical pH range for terrestrial carbonate producing systems is 8 to 9, meaning that most dissolved inorganic carbon (DIC) is present as bicarbonate. This means in most cases $[\text{CO}_3]_{(\text{aq})}^{2-}$ must be estimated from the Henderson-Hasselbach-like control on the second ionisation coefficient (k_2) within the DIC system exerted by the pH, which varies with temperature and ionic strength (Patterson et al., 1984)

$$20 \quad k_2 = 4 \times 10^{-7} T^2 - 1 \times 10^{-4} T^2 + 0.015T - \left\{ 0.095 \sqrt{l}^4 - 0.58 \sqrt{l}^3 + 1.51l - 1.82 \sqrt{l} + 10.63 \right\} \quad (9)$$

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Ultimately, we find that using this analytical approach G can be calculated from field-derived measurements of temperature, pH, $[\text{Ca}_{(\text{aq})}^{2+}]$, $[\text{HCO}_{3(\text{aq})}^-]$ (or $[\text{CO}_{3(\text{aq})}^{2-}]$ where $\text{pH} > 10$) and ionic strength (i.e. the sum of all charge arising from dissolved ions), which is a dataset that can be reasonably created for any new system.

Although G is a fundamentally important parameter controlling the potential rate of reaction between the ions in solution and solid precipitates, it primarily represents the likelihood of the system to overcome the activation energy of the crystallisation reaction. It is therefore convenient to reduce it to a dimensionless index reflecting the likelihood of spontaneous nucleation of calcite. Experimentally-derived values for the activation energy of spontaneous calcite nucleation are $48.1 \pm 4.3 \text{ kJ mol}^{-1}$ (Inskeep and Bloom, 1985). For our final classification we will use the dimensionless “Spontaneous Nucleation Index” (“SNI”) in preference to the dimensional G . It should be noted that as activation energy will be considerably reduced at any available solid surface, and particularly those surfaces that provide suitable templates for formation of calcite, nucleation in dirty and complex field settings will be considerably below this value, so rapid precipitation will straightforwardly occur at SNI values well below 1.

A potentially critically important, first-order parameter controlling the biological components the presence of which will affect the water: precipitate system is temperature. At high temperature (typically over 40°C), macrophytes are excluded leaving only microbial processes to interact with mineral precipitation. At temperatures above $\sim 60^\circ\text{C}$, biofilms will be dominated by thermophyles, diversity falls and the potential for biomediated precipitation will thus be altered.

We therefore propose that – to first-order – sites can be classified in a binary sense according to their SNI and water temperature, and our analysis will therefore focus primarily on the impact of high/low entropy (SNI) versus high/low enthalpy (T).

2.1 Compilation of field data

We do not pretend that the compilation of field data presented here is in any way comprehensive, and simultaneously recognise the advantage to future classification

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schemes if it were more comprehensive. We therefore link this paper to an online resource to which further data can be added, calculations are performed using a single set of equations and calculated parameters added to our database (URL will be inserted here). The field data used in the subsequent analyses are summarised in Table 2, which shows the wide range of compositions of near neutral-alkaline spring waters occurring in nature. To simplify this disparate data, a number of sub-populations are classified in terms of region of occurrence and water temperature (Table 2). Variance within these sub-populations remains quite high, with calcium concentration in cold Turkish springs varying by nearly 300 % of the mean (Table 2). Ionic strength, which is only partially dependant on the position of a location relative to source, is the most constant; ionic strength in the water at Plitvice varies only by about 10 % of the mean despite this being a relatively large dataset ($n = 65$). Even with the simplification provided by regional grouping, the data remain markedly unstructured in terms of the relationships between key parameters such as calcium and carbonate concentrations (Fig. 1a) or temperature and ionic strength (Fig. 1b), all of which vary independently.

Comparison of water temperature and the SNI (Fig. 2) does not result in more structure within the data, but it does result in better clustering of the data than individual ion concentrations, as sites can differ between very high carbonate ion but low calcium ion concentration (e.g. Mono Lake) and vice versa (many Italian springs). The thermodynamic approach therefore provides a suitable simplification of the data for further analysis.

3 Towards linking process to product

The first-order analysis of sites based on entropy versus enthalpy proposed above is shown in Fig. 3. There is a natural clustering of data in the region of the origin, reflecting the relatively high abundance of data from “meteoene” sources within non-tectonic karstic regions. Nevertheless, our collection of field data does encompass the majority of entropy: enthalpy space reasonable to expect from natural systems. We first report

a case study from each quartile of the diagram, then highlight some key features of the transition zones between (e.g. between “hot” and “cold” systems) and on the edges (e.g. at the lower limit of significant carbonate production) of these quartiles.

3.1 “Hot, non-biomediated” systems with high enthalpy and entropy

5 Example: La Zitelle, Italy; Terme San Giovanni, Italy

Informally – “Super-Travertine”

10 In these systems, Gibbs free energy is high enough for only moderate assistance to be required for precipitation and biota are restricted to thermophile microbes by high water temperature. Precipitation will be rapid and without material control from biological activity.

15 In high temperature thermal sites, calcium carbonate saturation levels are too extreme for any macrophytes or thermophile microbial biofilm development (Fig. 4). Such extreme hydrothermal waters degas rapidly immediately upon resurgence and this triggers a very rapid precipitation of calcite which nucleates onto the substrate, which provides surfaces with reduced activation energy further permitting the reaction (Fig. 4a, d, e). Such spontaneous crystalline precipitates typically consist of palisade stands of sparite crystals with their *C* axes oriented normal to substrate and with individuals from
20 1–60 mm long (Fig. 4c). Clusters of calcite rosettes are also common. Crystal length appears to be controlled by water depth suggesting that standing pools best encourage this development. However, macroscopic rhombic calcite crystals also nucleate rapidly on the bottom of fast-flowing gutters to form complex fanning twins with overall botryoidal morphologies (Fig. 4b). When followed away from resurgence points these
25 fabrics progressively give way to microbial dominated travertine and ultimately to ambient temperature paludal tufa laminites with dense macrophyte associations (Fig. 4d).

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In these systems, Gibbs free energy is sufficiently high for only moderate assistance being required for precipitation. Biota *may* be abundant and diverse, but extreme composition of the water may also be limiting via toxicity. Regardless, abiotic mineral precipitation is dominant and sufficiently rapid for biological influence to be minor and therefore masked in resulting deposits.

Extremely high alkalinity in these environments leads to continuous pelagic lime mud precipitation which often results in a milky to pale turquoise colour to the water even during cooler periods (Fig. 6). Aquatic organisms are generally excluded from such waters due to the extremely high precipitation rates which choke gill-breathing organisms and deeply encrust vegetation in precipitates after only a few hours. The host waters, however, may not be toxic and extensive marginal vegetation may develop throughout the system (Pedley, 2000). Biofilms are thin and discontinuous and mainly located on the narrow spill-over points of rimstone pools in the paludal areas and in broader botryoidal areas of barrage growth across the outflowing watercourses (Fig. 6a). Precipitates are rapid with extensive development of rimstone pools each forming broad terracettes separated by narrow sinuous crested micro-dams. Pool depths in the paludal areas are generally a few centimetres deep and are infilled with lime muds (Fig. 6b, c). These muds are generated by precipitation within the pool areas and may be massive or finely laminated. Lithification generally is absent in the pool deposits and only weak within the rimstone dam areas. At faster flowing sites small transverse barrages of weakly lithified lime mud laminites develop into broad, vertical to overhanging botryoidal walls which impound small, deep pools floored with unlithified lime muds. These muds are typified by bizarre, micro-crystalline calcite growth-forms typified by imperfectly formed crystals, some with baroque faces, by hollow microspheres and by truncated skeletal crystal growth-forms. Tufa towers may grow under similar conditions within alkaline lakes (e.g. Mono Lake, USA). These vertical structures also exhibit rapid growth fabrics with occasional microbial laminations but are essentially inorganic carbonate precipitates.

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3.4 “Cold, biomediated” systems with low enthalpy and entropy

For example: Plitvice, Croatia

Informally – “Tufa”

5 These are the classic, karstic tufa systems and are the most widespread form of terrestrial carbonate. Gibbs free energy is too low to allow spontaneous nucleation, so that precipitation is dependent on some mechanism allowing the activation energy to be reduced. Biota are abundant and diverse, permitting the full range of biomediation mechanisms to be active.

10 These deposits (Fig. 7) are extensively developed in association with phytoherm framestones in fluvial perched springline, paludal and lacustrine settings (Pedley, 1990). Biofilms are developed on all available surfaces and all actively precipitate thick calcium carbonate laminae often composed of alternations of spar and micrite cements and commonly developed into stromatolitic growths (Fig. 7a). Micritic precipitates with a characteristic laminar or peloidal texture may also dominate the system (Fig. 7b, c). A diverse range of invertebrates, vertebrates and vegetation are always associated with these sites. Precipitates rapidly lithify and progressively entomb earlier biomediated areas. Typically, they aggrade and prograde into lithofacies scale deposits (Fig. 7c) which bury macrophytes and are capable of infilling valleys. These impound bodies of water from pond to lake scale (Fig. 7d) within which further pelagic precipitation occurs and regularly laminated lake floor lime muds accumulate which may be associated with sapropels.

3.5 Interfacial systems with temperature in the region 30–40 °C

25 These deposits show overlapping similarities with travertine and tufa systems, and are likely to show interfingering of facies stratigraphically at individual sites. The most important impact of this in terms of product is that aquatic macrophytes are likely to be

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excluded by the high temperature, but may periodically establish when/where the temperature threshold (ca. 30 °C) is reached. Microbiota may be abundant and diverse depending on local ecological factors, but the composition of biofilms will differ from systems developing at lower temperatures. Diatoms grow best at temperatures < 35 °C and photosynthetic elements of biofilms above this temperature will be dominated by cyanobacteria (Blanchard et al., 1996) meaning that the metabolic functioning of biofilms will alter through the 30–40 °C temperature range.

These deposits manifest in an abundance of thermophile and ambient temperature microbial colonisers associated with scattered, small cushion-shaped phytoherms (often single species of grass) throughout (Fig. 4a, b). There is also a marked tendency for laminite development, partially arising from the flow conditions of these sites which are typically found on the outermost gently inclined parts of travertine sheets and distal margins of thermal fissures (Fig. 4a). Here, the virtually ambient temperature of the outflowing former-hydrothermal waters is sufficiently low to permit scattered macrophyte colonisation. Figure 4b shows a profile view of the colonisers in Cava Oliviera quarry. Note the non-preservation of roots and the thick accumulation of laminites around the vegetation. In some instances over 100 mm of laminate accumulation has occurred during the lifetime of individual plants, which attests to high entropy in these cases.

3.6 Interfacial systems with moderate SNI

In close analogy with temperature, systems which are marginal in terms of SNI will present mixed petrologies and geomorphologies from the high and low entropy type systems. Again in close analogy with high enthalpy systems, high entropy systems will inevitably evolve into low entropy systems in time and space. However, the SNI range this transition will occur at is not well determined by our data, due to lack of specifically collected field petrographic evidence, beyond a general indication it will lie at SNI ~ 0.2. This transition is an interesting target for future field research.

In terms of product, biomediated and physico-chemical type-products will interfinger both in time and space in these interfacial systems, in the same manner that high

and low enthalpy products interfinger in time and space in thermal interfacial systems. Again, there is a lack of field data concerning the diagnosis of these entropic transition zones.

3.7 Defining the thermodynamic lower boundary of terrestrial carbonate precipitation

In these marginal systems where there is insufficient Gibbs Free Energy for calcite to nucleate spontaneously, precipitation will largely if not exclusively be biomediated. Consequently, at high temperatures where waters are too hot for macrophyte colonisation (although they may be extensively colonised by thermophilic microbial mats) and thus biomediation is limited, significant precipitates and petrographic data are sparse. Any carbonate precipitates will be thin and slow to develop. Typically, thin calcite rafts floating on the surface of resurgence pools are the only tangible precipitates (Fig. 8a). Progressively as the precipitate slowly develops these rafts become too heavy to be held on the meniscus and they sink to produce chaotic pseudo-floe calcite sheet debris.

At low temperature, an extensive development of biofilm will coat available substrates (Fig. 9a, b) but precipitates will tend to be restricted to thin discontinuous micritic laminae. Generally, in cooler humid climatic situations these developments are localised to resurgence points, the resurgences sometimes being identified by a very restricted patch of thin tufa in its immediate vicinity (Fig. 9c). Commonly the carbonate precipitates are not visible in the field, but can be viewed by binocular microscope as whitish films or particulate micrite on and within the biofilm surface. A diverse range of biota is associated with these sites. A common type of development in the Yorkshire dales and in Belgium is associated with “Cron”-type sites (Pentecost, 2005) where discontinuous biofilms develop in the capillary zone on the surface of grass or moss cushions. The micrite precipitates may lithify into thin delicate sheets or may constantly wash or fall from these vertical surfaces and develop into peripheral detrital lime mud deposits. In flowing waters there is a common tendency for marginal systems to be associated with thin calcite films precipitated in association with epiphyllous algae on the under surface

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of river weed such as *Potamogetum*. Superficial oncoids in which a few thin skins of carbonate are wrapped around suitable sized clastic nuclei are another common association of sub-tufa environments (Fig. 9a, b).

However, we do not find that it is possible to draw a horizontal line on Fig. 3 dividing sites precipitating significant and insignificant carbonate. This echoes a previous assessment of surface water in the Yorkshire Dales (UK), where no spatial relationship between water chemistry and precipitate occurrence could be identified (Pentecost, 1992) and other efforts in which precipitation was simultaneously present and absent in hydrochemically similar sites (Hagele et al., 2006; Ledger et al., 2008). Thus, we do not find the failure of thermodynamics to determine this boundary a surprising result; as SNI decreases and biomediation becomes more important to carbonate creation, small-scale variations in SNI will inevitably become immaterial. Clearly another direction is needed to determine this boundary.

4 Towards a new paradigm for defining the lower limit on carbonate precipitation at low SNI

As biofilms play a demonstrable role in promoting calcite precipitation (Bissett et al., 2008a; Shiraishi et al., 2008a, b; Pedley et al., 2009; Rogerson et al., 2008) and typically demonstrate more a tendency to alter the macroenvironment rather than be altered by it (Rogerson et al., 2010; Bissett et al., 2008b) it is clear that a non-thermodynamic paradigm for the process determining the lower limit of terrestrial carbonate precipitation will arise from better understanding of microbial processes. This will require a fundamental re-assessment of how fieldwork in these systems is performed, as even rather basic microbiological information is very seldom collected for terrestrial carbonate systems. Using a case study from Lincolnshire (UK) (Fig. 10), we propose a potential way forward.

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4.1 Lincolnshire case study; demonstrating the coincidence of high microbial activity and precipitation of significant carbonate in “borderline” systems

In this case study, we emphasise the failure of thermodynamic assessments to determine the lower boundary of significant terrestrial carbonate production, and simultaneously attempt to link that boundary to a relatively simple assessment of on-site microbial activity. Although probably not significant players in biomediation of precipitate, local maxima in the suspended bacterial count will reflect locally enhanced productivity. This close association of higher biomass and diversity at tufa sites relative to non-tufa sites is not our suggestion, but a known feature of these systems (Marks et al., 2006). To incorporate a simple microbiological measurement to the classification framework we propose here, we use suspended bacterial count as a proxy for the ecological energy flux (Marks et al., 2006) in the same way that water chemistry measurements traditionally act as a proxy for the gradient of thermodynamic forcing (see Sect. 2).

4.1.1 Background information on sites

Annual rainfall in Lincolnshire is 577 mm, and average summer and winter air temperatures are 18 and 5 °C, respectively. The first location, Stainton le Vale (UK Grid reference TF17622 BNG93804; Fig. 10), lies on the Cretaceous chalk Wold hills and aquifer water emerges from two springs positioned a few meters apart at the base of a quartzarenite bed that occurs within the Chalk. Limited carbonate precipitation occurs along the stream banks and onto the biofilm-encrusted carbonate surfaces of a small (1.5 m high) tufa cascade (Fig. 11). Three sites have been studied from this valley; S1 is upstream near the springs where there is no geomorphologically significant carbonate forming, S2 is adjacent to the waterfall where crystalline patches of older carbonate outcrop at the water surface/stream bank interface but is barely producing a significant “tufa” product, S3 is downstream where the stream emerges from woods and flows through cultivated land, and no deposition is evident. The second location is at Waddingham, which lies on the eastern side of the Lincolnshire Edge Jurassic

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limestone hills (UK Grid Reference SK96457 BNG95311; Fig. 10). Again three sites were studied, one of which shows discontinuous oncoid development (W2) and two which are respectively immediately upstream and immediately downstream of the oncoid site (W1 and W3) and produce no significant precipitation. All six sites are included in preceding figures as “Lincolnshire sites”.

The precipitate at site S2 is a friable, porous deposit adhering to the outer surface of siliciclastic stream bank muds. The precipitate is closely associated with organic matter, moss, fungi, heterotrophic bacteria and cyanobacteria from stream waters and surrounding vegetation. Microscopic grains cemented into the carbonate fabric enable small scale aggradational seasonal laminae to be seen (Fig. 11). The sheet-like morphology of both precipitate and biofilm laminae consist of alternative clotted micrite and spar calcite. The degree of lithification, scarcity of detrital grains and association with organic components together identify this deposit as a tufa according to the terminology first proposed by Pedley (1994).

4.1.2 What makes the Tufa site “Stainton 2” (S2) different from the other non-product producing sites (S1, S3 and W 1–3)?

Counter-intuitively, calcium (up to 490 mg L^{-1} ; Table 3) and bicarbonate (up to 880 mg L^{-1} ; Table 3) concentrations are all higher at Waddingham than at Stainton (up to 260 mg L^{-1} and up to 460 mg L^{-1} ; Table 3), presumably reflecting the source water being derived from friable limestone rather than the less solution-prone well lithified Chalk. Both pH (7.5–8.3) and magnesium concentrations (Table 3) were similar in both streams. It is therefore completely unsustainable to assume the tufa/sub-tufa boundary is controlled by the thermodynamic forcing of source waters; the simple water chemistry approach we otherwise advocate in this paper would indicate that Waddingham was more likely to be above the tufa to sub-tufa boundary than is Stainton. There must, therefore, be another mechanism dominating these systems which is not reflected within the water analyses.

space a precipitate reflects will underpin all subsequent investigation of that material and its environmental significance.

We do not currently have the information available to determine the SNI level at which non-biological precipitation begins to dominate, other than that this level appears to be in the region of 0.2. This is likely to be a fruitful avenue of research to pursue, as once determined different precipitation mechanics can securely be invoke to understanding the origin of a precipitate determined by whether the product appears to indicate conditions above or below this critical value.

We also do not have the information available to understand the lower limit of SNI at which significant precipitation takes place. Indeed, we find it is unlikely any such division can be determined, but that precipitation dynamics at this level is regulated by biology rather than purely physical processes. We emphasise this problem with a new case study. We also propose a simple field-based means of further investigation of the role of biology in regulating this system, and show that at sites of precipitation suspended cell count is up to an order of magnitude higher than adjacent reaches of the same river. This is also likely to be a fruitful avenue for future research.

Supplementary material related to this article is available online at <http://www.earth-surf-dynam-discuss.net/1/337/2013/esurfd-1-337-2013-supplement.pdf>.

References

- Anadon, P., Utrilla, R., and Vazquez, A.: Mineralogy and Sr-Mg geochemistry of charophyte carbonates: a new tool for paleolimnological research, *Earth Planet. Sc. Lett.*, 197, 205–214, 2002.
- Andrews, J. E.: Palaeoclimatic records from stable isotopes in riverine tufas: Synthesis and review, *Earth-Sci. Rev.*, 75, 85–104, 2006.

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Andrews, J. E., Gare, S. G., and Dennis, P. F.: Unusual isotopic phenomena in Welsh quarry water and carbonate crusts, *Terr. Nova*, 9, 67–70, doi:10.1111/j.1365-3121.1997.tb00004.x, 1997.

Bayari, C. S. and Kurttas, T.: Algae: An important agent in deposition of karstic travertines: Observations on natural-bridge Yerkopru travertines, Aladaglar, Eastern Taurids, Turkey, 5th International Symposium and Field Seminar on Karst Waters and Environmental Impacts, Antalya, Turkey, ISI:A1997BH23Q00034, 269–280, 1995.

Bissett, A., DeBeer, D., Schoon, R., Shiraishi, F., Reimer, A., and Arp, G.: Microbial mediation of tufa formation in karst-water creeks, *Limnol. Oceanogr.*, 53, 1159–1168, 2008a.

Bissett, A., Reimer, A., de Beer, D., Shiraishi, F., and Arp, G.: Metabolic Microenvironmental Control by Photosynthetic Biofilms under Changing Macroenvironmental Temperature and pH Conditions, *Appl. Environ. Microbiol.*, 74, 6306–6312, doi:10.1128/aem.00877-08, 2008b.

Blanchard, G. F., Guarini, J. M., Richard, P., Gros, P., and Mornet, F.: Quantifying the short-term temperature effect on light-saturated photosynthesis of intertidal microphytobenthos, *Mar. Ecol.-Prog. Ser.*, 134, 309–313, doi:10.3354/meps134309, 1996.

Brasier, A. T., Andrews, J. E., and Kendall, A. C.: Diagenesis or dire genesis? The origin of columnar spar in tufa stromatolites of central Greece and the role of chironomid larvae, *Sedimentology*, 58, 1283–1302, doi:10.1111/j.1365-3091.2010.01208.x, 2011.

Buccino, G., D'Argenio, B., Ferreri, V., Brancaccio, L., Ferreri, M., Panachi, C., and Stazione, D.: I travertini della basse valle del Tanagro (Campania), Studio geomorfologico, sedimentologico e geochimico, *Boll. Soc. Geol. Ital.*, 97, 617–646, 1978.

Carrara, C.: I travertini di Canino (Viterbo, Italia Centrale): elementi di cronolitostratigrafia, di geochimica isotopica e loro significato ambientale e climatico, *Quaternario*, 7, 73–90, 1994.

Carrara, C., Ciufarella, L., and Paganin, G.: Inquadramento geomorfologico e climatico-ambientale dei travertini di Rapolano Terme (SI), *Quaternario*, 11, 3119–3329, 1998.

Carthew, K. D., Taylor, M. P., and Drysdale, R. N.: An environmental model of fluvial tufas in the monsoonal tropics, Barkly karst, northern Australia., *Geomorphology*, 73, 78–100, 2006.

Chafetz, H. S. and Folk, R. L.: Travertines – Depositional morphology and the bacterially constructed constituents, *J. Sediment. Petrol.*, 54, 289–316, 1984.

Chen, J. A., Zhang, D. D., Wang, S. J., Xiao, T. F., and Huang, R. G.: Factors controlling tufa deposition in natural waters at waterfall sites, *Sedimentary Geol.*, 166, 353–366, 2004.

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- Clark, I. D. and Fontes, J. C.: Paleoclimatic reconstruction in northern oman based on carbonates from hyperalkaline groundwaters, *Quaternary Res.*, 33, 320–336, 1990.
- D'Argenio, B. and Ferreri, V.: Ambiente di deposizione e litofacies dei travertino quaternari dell'Italia centrale-meridionale, *Mem Soc. Geol. It.*, 41, 861–868, 1988.
- 5 Dandurand, J. L., Gout, R., Hoefs, J., Menschel, G., Schott, J., and Usdowski, E.: Kinetically controlled variations of major components and carbon and oxygen isotopes in a calcite-precipitating spring, *Chem. Geol.*, 36, 299–315, 1982.
- Decho, A. W.: Overview of biopolymer-induced mineralization: What goes on in biofilms?, *Ecol. Eng.*, 36, 137–144, doi:10.1016/j.ecoleng.2009.01.003, 2010.
- 10 Dittrich, M. and Sibling, S.: Calcium carbonate precipitation by cyanobacterial polysaccharides, in: *Speleothems and Tufas: Unravelling Physical and Biological controls*, edited by: Pedley, H. M. and Rogerson, M., Geological Society of London Special Publication, Geological Society of London, London, 2010.
- Dramis, F., Materazzi, M., and Cilla, G.: Influence of climate change on freshwater travertine deposition: a new hypothesis, *Phys. Chem. Earth*, 24, 893–897, 1999.
- 15 Dreybrodt, W. and Buhmann, D.: A mass-transfer model for dissolution and precipitation of calcite from solutions in turbulent motion, *Chem. Geol.*, 90, 107–122, 1991.
- Dreybrodt, W., Eisenlohr, L., Madry, B., and Ringer, S.: Precipitation kinetics of calcite in the system $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$: The conversion to CO_2 by the slow process $\text{H}^++\text{HCO}_3^-\rightarrow\text{CO}_2+\text{H}_2\text{O}$ as a rate limiting step, *Geochim. Cosmochim. Ac.*, 61, 3897–3904, 1997.
- 20 Drysdale, R. N. and Gale, S. J.: The Indarri Falls travertine dam, Lawn Hill Creek, northwest Queensland, Australia, *Earth Surf. Proc. Land.*, 22, 413–418, 1997.
- Drysdale, R., Lucas, S., and Carthew, K.: The influence of diurnal temperatures on the hydrochemistry of a tufa-depositing stream, *Hydrol. Process.*, 17, 3421–3441, 2003a.
- 25 Drysdale, R. N., Carthew, K. D., and Taylor, M. P.: Larval caddis-fly nets and retreats: a unique biosedimentary paleocurrent indicator for fossil tufa deposits, *Sediment. Geol.*, 161, 207–215, doi:10.1016/s0037-0738(03)00114-3, 2003b.
- Dunham, R. J.: Classification of carbonate rocks according to depositional texture, in: *Classification of Carbonate Rocks*, edited by: Ham, W. E., *Am. Assoc. Petrol. Geol.*, Tulsa, Oklahoma, 108–121, 1962.
- 30 Dupraz, C., Reid, R. P., Braissant, O., Decho, A. W., Norman, R. S., and Visscher, P. T.: Processes of carbonate precipitation in modern microbial mats, *Earth-Sci. Rev.*, 96, 141–162, doi:10.1016/j.earscirev.2008.10.005, 2009.

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- Embrey, A. F. and Kloven, E. J.: Absolute water depth limits of Late Devonian paleoecological zones, *Geol. Rundsch.*, 61, 672–686, 1972.
- Emeis, K. C., Richnow, H. H., and Kempe, S.: Travertine Formation in Plitvice-National-Park, Yugoslavia – Chemical Versus Biological-Control, *Sedimentology*, 34, 595–609, 1987.
- 5 Eremim, A., Bulychev, A., Krupenina, N. A., Mair, T., Hauser, M. J. B., Stannarius, R., Muller, S. C., and Rubin, A. B.: Excitation-induced dynamics of external pH pattern in *Chara* corallina cells and its dependence on external calcium concentration, *Photoch. Photobio. Sci.*, 6, 103–109, doi:10.1039/b607602e, 2007.
- Ferreri, V.: Criteri di analisi facies e classificazione dei travertini pleistocenici dell'Italia meridionale, *Rend. Acc. Sci. Fis. Mat. Serie*, 4, 1–47, 1985.
- 10 Folk, R. L.: Practical petrographic classification for limestones, *Bull. Amer. Assoc. Petroleum Geologists.*, 43, 1–38, 1959.
- Folk, R. L.: Interaction between bacteria, nannobacteria and mineral precipitation in hot springs of Central Italy., *Geogr. Phys. Quatern.*, 48, 233–246, 1994.
- 15 Folk, R. L. and Chafetz, H. S.: Pisoliths (pisoids) in Quaternary travertines of Tivoli, Italy, in: *Coated Grains*, edited by: Peryt, T. M., Springer-Verlag, Berlin., 474–487, 1983.
- Folk, R. L., Chafetz, H. S., and Tiezzi, P. A.: Bizarre forms of depositional and diagenetic calcite in hot spring travertines, central Italy, in: *Carbonate Cements Soc.*, edited by: Schneidmann, N. B. and Harris, P., *Econ. Paleont. Miner. Spec. Publ.*, 349–369, 1985.
- 20 Ford, T. D. and Pedley, H. M.: Tufa and travertine deposits of the Grand Canyon, Cave and Karst Science, 24, 107–116, 1997.
- Glover, C. and Robertson, A. F. H.: Origin of tufa (cool water carbonate) and related terraces in the Antalya area, S.W. Turkey, *Geol. J.*, 38, 329–358, 2003.
- Golubić, S.: Cyclic and non-cyclic mechanisms in the formation of travertine, *Verh. Int. Ver. Theor. Ang. Limnol.*, 17, 956–961, 1969.
- 25 Golubić, S., Violante, C., Ferreri, V., and D'Argenio, B.: Algal control and early diagenesis in Quaternary travertine formation (Rocchetta a Volturno, Central Apennines, in: *Studies on Fossil Benthic Algae*, edited by: Barattolo, F., *Boll. Soc. Paleontol. Ital., Spec. vol.*, 231–247, 1993.
- 30 Guo, L. and Riding, R.: Hot spring travertine facies and sequences, Late Pleistocene Rapolano Terme, Italy, *Sedimentology*, 45, 163–180, 1998.

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Hammer, O.: Watch your step, *Nat. Phys.*, 4, 265–266, doi:10.1038/nphys915, 2008.

5 Hammer, O., Dysthe, D. K., and Jamtveit, B.: The dynamics of travertine dams, *Earth Planet. Sc. Lett.*, 256, 258–263, 2007.

Hammer, O., Dysthe, D. K., Lelu, B., Lund, H., Meakin, P., and Jamtveit, B.: Calcite precipitation instability under laminar, open-channel flow, *Geochim. Cosmochim. Ac.*, 72, 5009–5021, doi:10.1016/j.gca.2008.07.028, 2008.

10 Hammer, Ø., Dysthe, D. K., and Jamtveit, B.: Travertine terracing: patterns and mechanisms, Geological Society, London, Special Publications, 336, 345–355, doi:10.1144/sp336.18, 2010.

Hobbie, J. E., Daley, R. J., and Jasper, S.: Use of Nuclepore filters for counting bacteria by fluorescence microscopy, *Appl. Environ. Microbiol.*, 33, 1225–1228, 1977.

15 Inskeep, W. P. and Bloom, P. R.: An evaluation of rate equations for calcite precipitation kinetics at pCO₂ less than 0.01 atm and pH greater than 8, *Geochim. Cosmochim. Ac.*, 49, 2165–2180, doi:10.1016/0016-7037(85)90074-2, 1985.

Irion, G. and Müller, G.: Mineralogy, petrology and chemical composition of some calcareous tufa from Swabische Alb, Germany, in: *Recent developments in carbonate sedimentology in Central Europe*, edited by: Müller, G., and Freidman, G. M., Springer-Verlag, 156–171, 1968.

20 Jones, B. and Renaut, R. W.: *Calcareous Spring Deposits in Continental Settings*, *Sedimentology*, 61, 177–224, 2010.

Julia, R.: Travertines, in: *Carbonate Depositional Environments*, edited by: Scholle, P. A., Bebout, D. G., and Moore, C., AAPG Mem., 64–72, 1983.

25 Kawaguchi, T. and Decho, A. W.: Isolation and biochemical characterization of extracellular polymeric secretions (EPS) from modern soft marine stromatolites (Bahamas) and its inhibitory effect on CaCO₃ precipitation, *Prep. Biochem. Biotech.*, 32, 51–63, 2002.

Kent, P., Gaunt, G. D., and Wood, C. J.: *British Regional Geology, Eastern England from the Tees to the Wash*, 2nd Edn., Institute of Geological Sciences, Natural Environment Research Council, HMSO, London, 1980.

30 Kupriyanova, E., Villarejo, A., Markelova, A., Gerasimenko, L., Zavarzin, G., Samuels-son, G., Los, D. A., and Pronina, N.: Extracellular carbonic anhydrases of the

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stromatolite-forming cyanobacterium *Microcoleus chthonoplastes*, *Microbiology*, 153, 1149–1156, doi:10.1099/mic.0.2006/003905-0, 2007.

Kupriyanova, E. V., Lebedeva, N. V., Dudoladova, M. V., Gerasimenko, L. M., Alekseeva, S. G., Pronina, N. A., and Zavarzin, G. A.: Carbonic anhydrase activity of alkalophilic cyanobacteria from soda lakes, *Russ. J. Plant Physl.*, 50, 532–539, 2003.

Ledger, M. E., Harris, R. M. L., Armitage, P. D., and Milner, A. M.: Disturbance frequency influences patch dynamics in stream benthic algal communities, *Oecologia*, 155, 809–819, doi:10.1007/s00442-007-0950-5, 2008.

Li, W., Yu, L. J., Yuan, D. X., Wu, Y., and Zeng, X. D.: A study of the activity and ecological significance of carbonic anhydrase from soil and its microbes from different karst ecosystems of Southwest China, *Plant Soil*, 272, 133–141, doi:10.1007/s11104-004-4335-9, 2005.

Li, W., Yu, L. J., Wu, Y., Jia, L. P., and Yuan, D. X.: Enhancement of Ca²⁺ release from limestone by microbial extracellular carbonic anhydrase, *Bioresource Technol.*, 98, 950–953, doi:10.1016/j.biortech.2006.03.021, 2007.

Liu, Z. H. and Dreybrodt, W.: Dissolution kinetics of calcium carbonate minerals in H₂O-CO₂ solutions in turbulent flow: The role of the diffusion boundary layer and the slow reaction H₂O+CO₂ reversible arrow H⁺⁺HCO₃, *Geochim. Cosmochim. Ac.*, 61, 2879–2889, 1997.

Liu, Z. H., Liu, X. L., and Liao, C. J.: Daytime deposition and nighttime dissolution of calcium carbonate controlled by submerged plants in a karst spring-fed pool: insights from high time-resolution monitoring of physico-chemistry of water, *Environ. Geol.*, 55, 1159–1168, doi:10.1007/s00254-007-1062-6, 2008.

Lorah, M. M. and Herman, J. S.: The chemical evolution of a Travertine-depositing stream: geochemical processes and mass transfer reactions, *Water Resour. Res.*, 24, 1541–1552, 1988.

Lowenstam, H. A.: Minerals formed by organisms, *Science*, 211, 1126–1131, 1981.

Marks, J. C., Parnell, R., Carter, C., Dinger, E. C., and Haden, G. A.: Interactions between geomorphology and ecosystem processes in travertine streams: Implications for decommissioning a dam on Fossil Creek, Arizona, *Geomorphology*, 77, 299–307, doi:10.1016/j.geomorph.2006.01.008, 2006.

Merz-Preiss, M. and Riding, R.: Cyanobacterial tufa calcification in two freshwater streams: ambient environment, chemical thresholds and biological processes, *Sediment. Geol.*, 126, 103–124, 1999.

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- Minissale, A.: Origin, transport and discharge of CO₂ in central Italy, *Earth-Sci. Rev.*, 66, 89–141, 2004.
- Nicod, J.: Repartition, classification, relation avec les milieux karstiques et karstification, *Bull. Assoc. Geogr. Fr.*, 479–480, 181–187, 1981.
- 5 Patterson, C. S., Busey, R. H., and Mesmer, R. E.: Second ionization of carbonic acid in NaCl media to 250°C, *J. Solution Chem.*, 13, 647–661, 1984.
- Pedley, H. M.: Classification and environmental models of cool freshwater tufas, *Sediment. Geol.*, 68, 143–154, 1990.
- Pedley, H. M.: Prokaryote microphyte biofilms: a sedimentological perspective, *Kaupia, Darmstader Betr. Naturgesch.*, 4, 45–60, 1994.
- 10 Pedley, H. M. and Rogerson, M.: In vitro investigations of the impact of different temperature and flow velocity conditions on tufa microfabric, in: *Speleothems and Tufas: Unravelling Physical and Biological controls*, edited by: Pedley, H. M. and Rogerson, M., Geological Society Special Publication, Geological Society of London, London, 193–210, 2010a.
- 15 Pedley, H. M. and Rogerson, M.: Introduction to tufas and speleothems, in: *Speleothems and Tufas: Unravelling Physical and Biological controls*, edited by: Pedley, H. M. and Rogerson, M., Geological Society Special Publication, Geological Society, London, 2010b.
- Pedley, H. M., Rogerson, M., and Middleton, R.: The growth and morphology of freshwater calcite precipitates from in Vitro Mesocosm flume experiments; the case for biomediation, *Sedimentology*, 56, 511–527, 2009.
- 20 Pedley, M.: Fresh-Water (Phytoherm) Reefs – the Role of Biofilms and Their Bearing on Marine Reef Cementation, *Sediment. Geol.*, 79, 255–274, 1992.
- Pedley, M., Andrews, J., Ordonez, S., delCura, M. A. G., Martin, J. A. G., and Taylor, D.: Does climate control the morphological fabric of freshwater carbonates? A comparative study of Holocene barrage tufas from Spain and Britain, *Palaeogeogr. Palaeoclimatol.*, 121, 239–257, 1996.
- 25 Peña, J. L., Sancho, C., and Lozano, M. V.: Climatic and tectonic significance of late Pleistocene and Holocene tufa deposits in the Mijares River canyon, eastern Iberian range, northeastern Spain, *Earth Surf. Proc. Land.*, 25, 1403–1417, 2000.
- 30 Pentecost, A.: Blue-green-algae and freshwater carbonate deposits, *P. Roy. Soc. Lond. B Bio.*, 200, 43–61, 1978.
- Pentecost, A.: Growth and calcification of the fresh-water cyanobacterium *rivularia*-haematites, *P. Roy. Soc. Lond. B Bio.*, 232, 125–136, 1987.

- Pentecost, A.: Carbonate Chemistry OF Surface Waters in a Temperate Karst Region – The Southern Yorkshire Dales, UK, *J. Hydrol.*, 139, 211–232, 1992.
- Pentecost, A.: Travertine, Springer, Berlin, 2005.
- Pentecost, A. and Lord, T. C.: Postglacial tufas and travertines from the Craven district Yorkshire, *Cave Science*, 15, 15–19, 1988.
- Pentecost, A. and Viles, H. A.: A review and reassessment of travertine classification, *Geogr. Phys. Quatern.*, 48, 305–314, 1994.
- Pentecost, A., Andrews, J. E., Dennis, P. F., Marca-Bell, A., and Dennis, S.: Charophyte growth in small temperate water bodies: Extreme isotopic disequilibrium and implications for the palaeoecology of shallow marl lakes, *Palaeogeogr. Palaeoclimatol.*, 240, 389–404, doi:10.1016/j.palaeo.2006.02.008, 2006.
- Plummer, L. N. and Busenberg, E.: The solubilities of calcite, aragonite and vaterite in CO₂-H₂O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O, *Geochim. Cosmochim. Ac.*, 46, 1011–1040, doi:10.1016/0016-7037(82)90056-4, 1982.
- Robinson, R. A. and Stokes, R. H.: *Electrolyte Solutions*, Second Revised Edition Edn., David and Charles, Newton Abbot, Devon, 2002.
- Rogerson, M., Pedley, H. M., Wadhawan, J. D., and Middleton, R.: New Insights into Biological Influence on the Geochemistry of Freshwater Carbonate Deposits, *Geochim. Cosmochim. Ac.*, 72, 4976–4987, 2008.
- Rogerson, M., Pedley, H. M., and Middleton, R.: Microbial Influence on Macroenvironment Chemical Conditions in Alkaline (Tufa) Streams; Perspectives from In Vitro Experiments, in: *Speleothems and Tufas: Unravelling Physical and Biological controls*, edited by: Pedley, H. M. and Rogerson, M., Geological Society Special Publication, Geological Society of London, London, 65–81, 2010.
- Saunders, P. V., Rogerson, M., Pedley, H. M., Wadhawan, J., and Greenway, G.: Mg/Ca ratios in freshwater microbial carbonates: Thermodynamic, Kinetic and Vital Effects, *Geochim. Cosmochim. Ac.*, in review, 2013.
- Schneider, J., Schneider, H. G., Campion, S. L., and Alsumard, T.: Algal micro-reefs-coated grains from freshwater environments, in: *Coated Grains*, edited by: Peryt, T. M., Springer, Berlin, 284–298, 1983.

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- Shiraishi, F., Bissett, A., de Beer, D., Reimer, A., and Arp, G.: Photosynthesis, respiration and exopolymer calcium-binding in biofilm calcification (Westerhfer and deinschwanger creek, germany), *Geomicrobiol. J.*, 25, 83–94, doi:10.1080/01490450801934888, 2008a.
- Shiraishi, F., Reimer, A., Bissett, A., de Beer, D., and Arp, G.: Microbial effects on biofilm calcification, ambient water chemistry and stable isotope records in a highly super-saturated setting (Westerhofer Bach, Germany), *Palaeogeogr. Palaeoclimatol.*, 262, 91–106, doi:10.1016/j.palaeo.2008.02.011, 2008b.
- Shiraishi, F., Zippel, B., Neu, T. R., and Arp, G.: In situ detection of bacteria in calcified biofilms using FISH and CARD-FISH, *J. Microbiol. Meth.*, 75, 103–108, doi:10.1016/j.mimet.2008.05.015, 2008c.
- Spiro, B. and Pentecost, A.: One Day in the Life of a Stream – a Diurnal Inorganic Carbon Mass Balance for a Travertine-Depositing Stream (Waterfall Beck, Yorkshire), *Geomicrobiol. J.*, 9, 1–11, 1991.
- Stirn, A.: Kalktuffvorkommen und Kalktufftypen der Schwäbischen Alb, *Abh. Karst Höhlenkd.*, 91, 1964.
- Symoens, J. J., Duvigneaud, P., and van den Bergen, C.: Aperçu sur la végétation des tufs calcaires de la Belgique., *Bull. Soc. R. Bot. Belg.*, 83, 329–352, 1951.
- Szulc, J.: Genesis and classification of travertine deposits, *Przegl. Geol.*, 31, 2311–2236, 1983.
- Tiziano, B.: Application of brine differentiation and Langelier–Ludwig plots to fresh-to-brine waters from sedimentary basins: Diagnostic potentials and limits, *J. Geochem. Explor.*, 108, 126–130, doi:10.1016/j.gexplo.2010.12.002, 2011.
- Veysey, J. and Goldenfeld, N.: Watching rocks grow, *Nat. Phys.*, 4, 310–313, doi:10.1038/nphys911, 2008.
- Visscher, P. T. and Stolz, J. F.: Microbial mats as bioreactors: populations, processes, and products, *Palaeogeogr. Palaeoclimatol.*, 219, 87–100, 2005.
- Wingender, J., Neu, T., and Flemming, H.-C.: What are Bacterial Extracellular Polymeric Substances?, in: *Microbial Extracellular Polymeric Substances*, edited by: Wingender, J., Neu, T., and Flemming, H.-C., Springer Berlin Heidelberg, 1–19, 1999.
- Zaihua, L., Svensson, U., Dreybrodt, W., Daoxian, Y., and Buhmann, D.: Hydrodynamic control of inorganic calcite precipitation in Huanglong Ravine, China: Field measurements and theoretical prediction of deposition rates, *Geochim. Cosmochim. Ac.*, 59, 3087–3097, 1995.

Table 1. Summary of microbial metabolic biogeochemistries, with full bicarbonate buffering. Adapted from (Visscher and Stolz, 2005).

Process	Non-calcite Reagents	Non-calcite Products	CaCO ₃ (s) per mole Carbon reacted	Microbial groups
Oxygenic photoautotrophy	$2\text{HCO}_3^-(\text{aq}) + \text{Ca}^{2+}(\text{aq})$	$\text{CH}_2\text{O}(\text{o}) + \text{O}_2(\text{aq})$	1	Cyanobacteria
Anoxygenic photoautotrophy	$3\text{HCO}_3^-(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + \text{HS}^-(\text{aq})$	$2\text{CH}_2\text{O}(\text{o}) + \text{SO}_4^{2-}(\text{aq})$	0.5	Purple and green sulphur bacteria
Aerobic respiration	$\text{CH}_2\text{O}(\text{o}) + \text{O}_2(\text{aq})$	$2\text{HCO}_3^-(\text{aq}) + \text{Ca}^{2+}(\text{aq})$	-1	Heterotrophic bacteria
Fermentation	$3\text{CH}_2\text{O}(\text{o}) + \text{H}_2\text{O}(\text{l})$	$2\text{HCO}_3^-(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{H}_6\text{O}(\text{aq})$	-0.2	Many organisms
Dissimilatory iron reduction	$\text{CH}_2\text{O}(\text{o}) + 4\text{FeO}_2\text{H}(\text{aq}) + 7\text{Ca}^{2+}(\text{aq}) + 6\text{HCO}_3^-(\text{aq})$	$4\text{Fe}^{2+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$	7	Iron reducing bacteria
Dissimilatory nitrate reduction	$5\text{CH}_2\text{O}(\text{o}) + 4\text{NO}_3^-(\text{aq})$	$6\text{HCO}_3^-(\text{aq}) + 2\text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{Ca}^{2+}(\text{aq})$	-0.2	Nitrate reducing bacteria
Sulphate reduction	$2\text{CH}_2\text{O}(\text{o}) + \text{SO}_4^{2-}(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + \text{OH}^-(\text{aq})$	$\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{HS}^-(\text{aq})$	0.5	Sulphate reducing bacteria ¹
Lithautotrophic Sulphate reduction	$8\text{H}_2(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{HCO}_3^-(\text{aq}) + 2\text{Ca}^{2+}(\text{aq})$	$\text{HS}^-(\text{aq}) + \text{CH}_3\text{CO-SCoA} + 3\text{H}_2\text{O}(\text{l})$	2 moles per mole of sulphur reduced	Lithautotrophic sulphate reducing bacteria
Aerobic sulphide oxidation	$\text{HS}^-(\text{aq}) + \text{O}_2(\text{aq})$	$\text{SO}_4^{2-}(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + \text{HCO}_3^-(\text{aq})$	-0.5 moles per mole of sulphur oxidised	Sulphide-oxidising chemolithoautotrophic bacteria
Anaerobic sulphide oxidation	$5\text{HS}^-(\text{aq}) + 8\text{O}_3^-(\text{aq}) + 3\text{HCO}_3^-(\text{aq}) + 3\text{Ca}^{2+}(\text{aq})$	$4\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l}) + 5\text{SO}_4^{2-}(\text{aq})$	0.6 moles per mole of sulphur oxidised	Sulphide-oxidising chemolithoautotrophic bacteria
Ammonium oxidation	$\text{NH}_4^+(\text{aq}) + 1.5\text{O}_2(\text{aq})$	$\text{NO}_2^-(\text{aq}) + 2\text{HCO}_3^-(\text{aq}) + 2\text{Ca}^{2+}(\text{aq})$	-2 ²	Ammonium-oxidising chemolithoautotrophic bacteria

¹ Can be up to 1.5 moles CaCO₃ per mole of carbon oxidised with certain “complete oxidation” metabolisms.

² Balanced by precipitation of 1 mole per mole of carbon fixed from CO_{2(aq)} via the Calvin cycle.

NB: other metabolic mechanisms such as two-step sulphide oxidation could be relevant, but only via variable microdomain ecology.

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Table 2. Summary of field data.

Type of System	<i>T</i>	SD	Ca	SD	CO ₃	SD	ϕ	SD	<i>n</i>
Alkaline lake (Mono)	8.503448	2.817101	4.96E-05	2.44E-05	0.218264	0.233316	0.32693	0.079703	29
Japanese spring	13.55385	3.593423	0.001636	0.000784	1.03E-05	8.6E-06	0.060093	0.034254	13
Semi-arid temperate tufa river (Ruidera)	13	9.899495	0.001559	0	5.39E-06	1.55E-06	0.037268	0.020361	2
Cool-humid temperate tufa river (Ddol)	10.09167	1.60055	0.002536	0.000198	1.2E-05	8.53E-06	0.110217	0.009203	4
Cool Italian spring (<20 °C)	11.74603	2.368941	0.002481	0.001755	3.85E-06	3.61E-06	0.024395	0.05971	63
Warm Italian spring (20–30 °C)	24.31818	2.868322	0.010117	0.00338	5.51E-06	4.95E-06	0.121783	0.040094	22
Thermal Italian spring (30–45 °C)	36.47619	4.434175	0.014957	0.005753	8.41E-06	1.19E-05	0.170503	0.04914	21
Hot Italian spring (> 45 °C)	53.48462	5.491182	0.015617	0.003252	1.15E-05	1.07E-05	0.235112	0.049828	13
Cool Turkish spring (<20 °C)	26.125	13.20795	0.000992	0.002949	0.017752	0.025325	0.311055	0.109201	43
Warm Turkish spring (20–30 °C)	21.125	1.314978	0.000468	0.000138	0.036236	0.047156	0.395252	0.042229	4
Thermal Turkish spring (> 30 °C)	42	3.016621	0.00214	0.004844	0.015501	0.012429	0.323649	0.120805	6
Warm-Humid temperature river (Plitvice)	12.04	3.518336	0.001197	0.000216	2.49E-05	1.25E-05	0.088541	0.038596	65
Oncoid-bearing rivers	9.920548	2.776537	0.002563	0.001029	9.77E-06	5.51E-06	0.076664	0.042811	72
Hot silica spring	88.25	20.83467	0.000603	0.001152	0.000864	0.001437	0.078981	0.039254	4

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Table 3. Mean field data for sites at Stainton and Waddingham, Lincolnshire, UK.

Location	pH	water temp (°C)	air temp (°C)	humidity %	flow rate m s ⁻¹	Ca mg L ⁻¹	Mg mg L ⁻¹	HCO ₃ ⁻ mg L ⁻¹	CO ₃ ²⁻ mg L ⁻¹	NO ₃ ⁻ mg L ⁻¹	PO ₄ ³⁻ mg L ⁻¹	DOC mg L ⁻¹	Cell count per ml
Waddingham 1	8.1	10.3	10.7	76.5	0.2	140.4315	1.38533	172.75	12.5	<10	1.7	5.5	1325
Waddingham 2	8.1	10.3	11.9	73.5	0.3	130.0203	1.818245	168.5	17.7	<10	0.7	5.6	1228
Waddingham 3	7.8	10.4	12.3	73.9	0.4	117.5268	1.154441	170.25	7.8	<10	2	5.9	1131
Stainton 1	7.7	9.5	11.6	72.3	0.4	80.56692	5.714484	91.5	0	<10	1.8	7.3	3490
Stainton 2	8	9.5	11.5	76.6	0.3	78.48468	3.607629	93.5	7.7	<10	1	7.3	22617
Stainton 3	8.1	9.5	11.7	76.6	0.3	72.95871	3.261297	93.5	10	<10	1.9	6.8	3134

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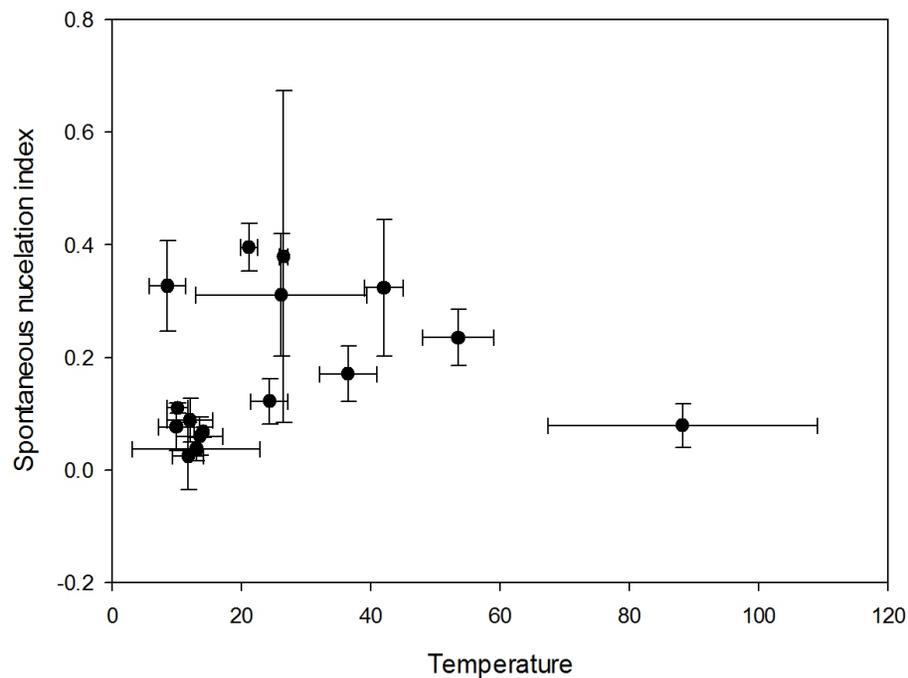


Fig. 2. Summary of spontaneous nucleation index (dimensionless) and temperature (°C) from Table 2 (note exponential scales).

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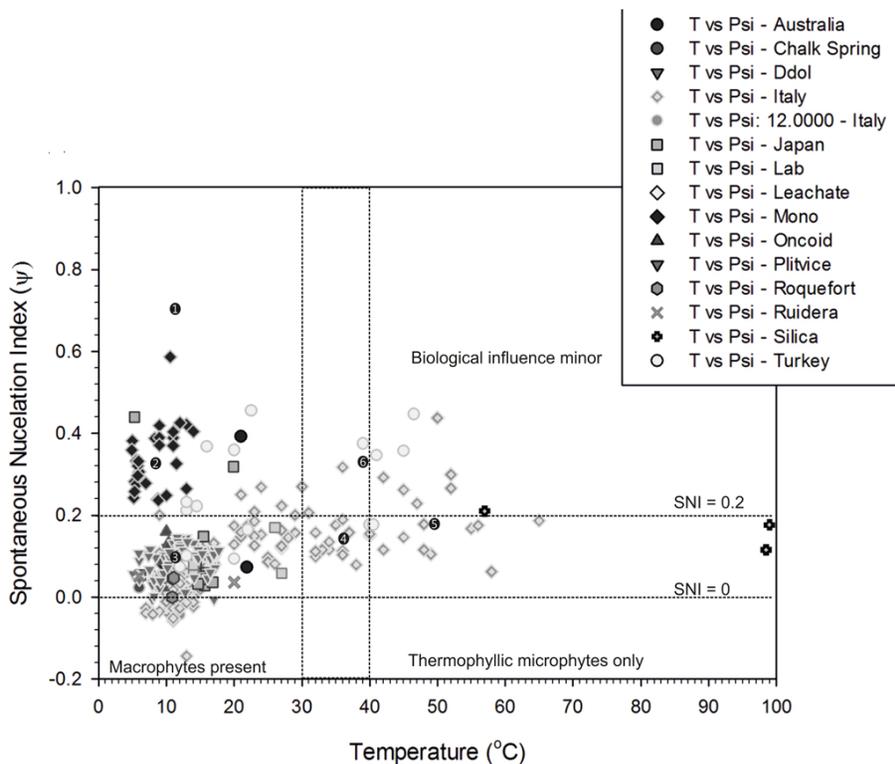


Fig. 3. Summary of travertine and tufa springwater chemistries on thermodynamic grounds (see Sect. 3). 1 = Brook Bottom (Sect. 3.3), 2 = Mono Lake (Sect. 3.3), 3 = Plitvice (Sect. 3.4), 4 = Terme di Saturnia (Sect. 3.2), 5 = Doccio (Sect. 3.2), 6 = Terme san Giovanni (Sect. 3.1).

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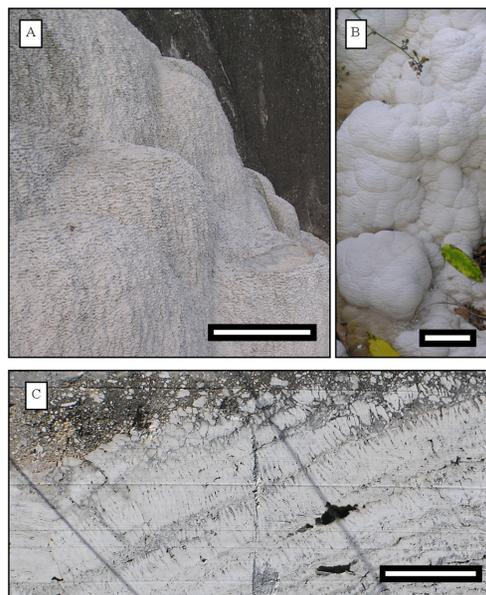


Fig. 4. High enthalpy and entropy. **(A)** Travertine build-up at the outflow point from the spar pool. Steep gradient microterraces are typical of the deposit. Scale bar is 1 m long. Terme San Giovanni, Tuscany, Italy. **(B)** Crystalline calcium carbonate in botryoidal masses lining an outflow channel. Scale bar is 100 mm long. Terme San Giovanni, Tuscany, Italy. **(C)** Palisade calcite growing normal to substrate within a Holocene travertine site. The sequence is capped by a palaeosol. Scale bar is 300 mm long. Terme San Giovanni, Tuscany, Italy. **(D)** Resurgent point at the Il Bollore spring. The hot emergent water is colonised with thermophilic bacteria. Around the margins, however, the temperature has fallen below 30 degrees and is colonised by phototrophic bacteria and algae (dark band). Il Bollore Spring, upper part of the Bagno San Filippo travertine complex, Amiata San Filippo, Italy **(E)** Balena Bianca travertine, lower part of the San Filippo travertine complex, Amiata San Filippo, Italy.

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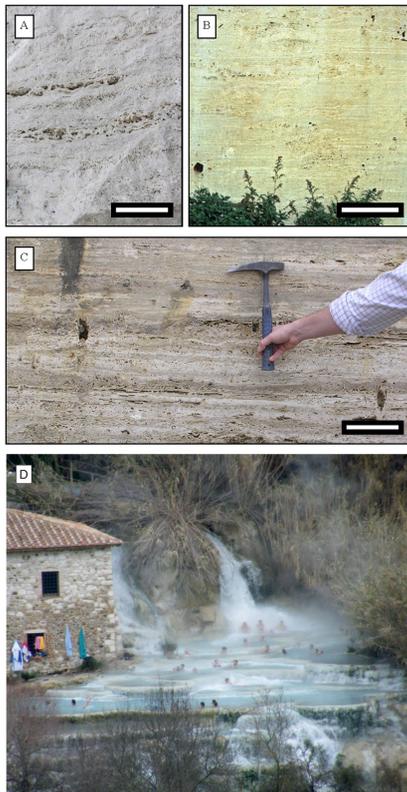


Fig. 5. High enthalpy, low entropy. **(A)** Laminated travertine with alternating bubble and laminate layering. Scale bar is 50 mm long. Holocene, Cava Oliviera, Tuscany, Italy. **(B)** Laminite-filled pools bounded by bacterial microherm dominated pool rims. Scale bar is 150 mm long. Early Quaternary Alcamo travertine, Sicily, Italy. **(C)** Typical laminated microbial travertine fabric. Scale bar is 150 mm long. Holocene Cava Oliviera, Tuscany, Italy. **(D)** Typical rim pool system from Saturnia, Tuscany, Italy. Note swimmers for scale, and steam rising from warm water (with thanks to Enrico Cappezuoli).

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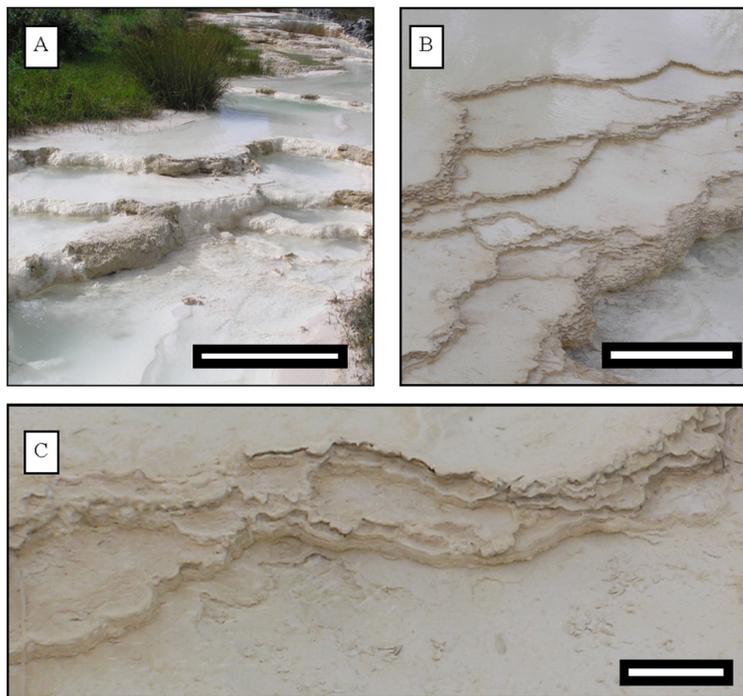


Fig. 6. Low enthalpy, high entropy. **(A)** Terrace and pool morphology in an active ambient temperature deposit. Note the large volume of lime mud within the pools. Scale bar is 1 m long. Brook Bottom, near Buxton, Derbyshire, UK. **(B)** Detail of the terracettes developed in gentle gradient sites. Note how the large upstream pools progressively overstep the smaller downstream features and progressively encourage the development of steps. Scale bar is 0.5 m long. Active, Brook Bottom, near Buxton, Derbyshire, UK. **(C)** Fine detail of the narrow pool rims and spillovers. Scale bar is 100 mm long. Brook Bottom, near Buxton, Derbyshire, UK.

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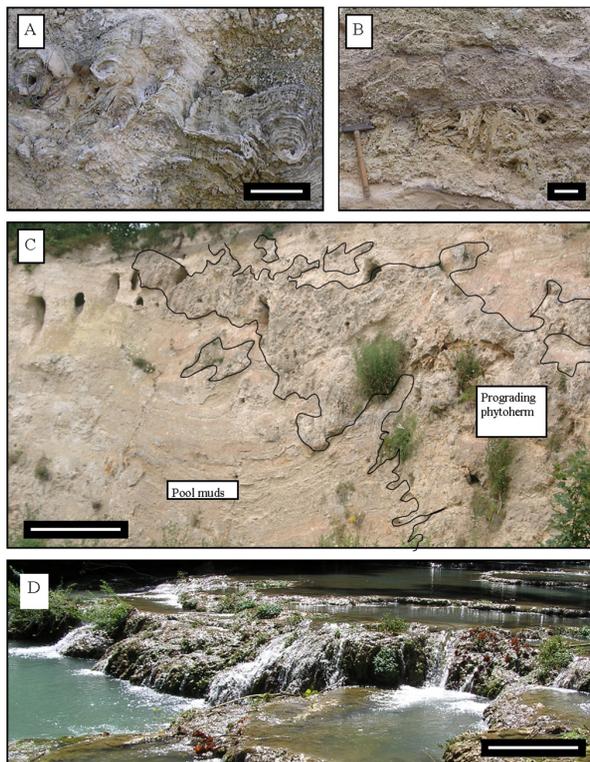


Fig. 7. Low enthalpy, low entropy. **(A)** Stromatolite microherm development in a fluvial tufa. Scale bar is 50 mm long. Early Quaternary Noto Tufa, Sicily, Italy. **(B)** Burr reed Phytotherm cushion interlayered with detrital tufas above and lacustrine lime muds below. Scale bar is 150 mm long. Holocene Caerwys tufa, North Wales. **(C)** Profile view of a prograding phytotherm framestone sandwiched between adjacent lime mud pool deposits. Scale bar is 150 mm long. Holocene Caerwys tufa, North Wales. **(D)** An active pool and barrage system forming in Tuscany. Scale bar is 1 m long. Colle val d’Elsa, Italy.

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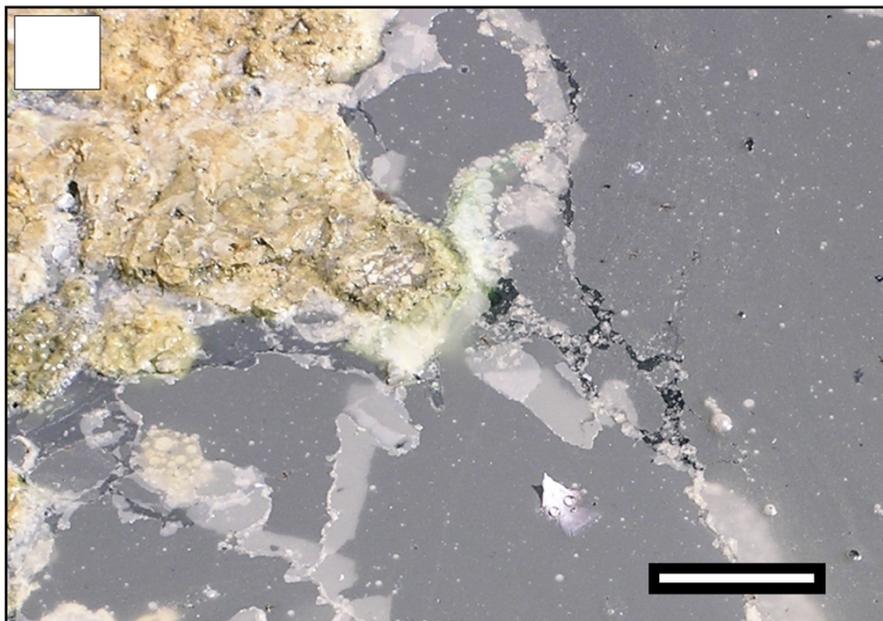


Fig. 8. Marginally precipitating systems under high enthalpy. Living biofilm associated with superficial skins of calcite. Note the thin calcite rafts at the air/water interface. This is the only observable precipitate at the site. Scale bar is 100 mm long. Recent, Petreole, Tuscany.

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Fig. 9. Marginally precipitating systems under low enthalpy. **(A)** Oncoids in a flowing water shallow stream without any other tufa association. Scale bar is 150 mm long. Welton Beck, Yorkshire, UK. **(B)** Close up of oblate shaped oncoids with a characteristic greyish green colour. Note the absence of any detrital tufa between the oncoids. Scale bar is 20 mm long. Welton Beck, Yorkshire, UK. **(C)** Small area of framework phytotherm tufa (granular area between macrophytes) in the immediate vicinity of one of the resurgence points of Welton Beck. Tufa is absent from the rest of the watercourse. Scale bar is 50 mm long. Welton Beck, Yorkshire, UK.

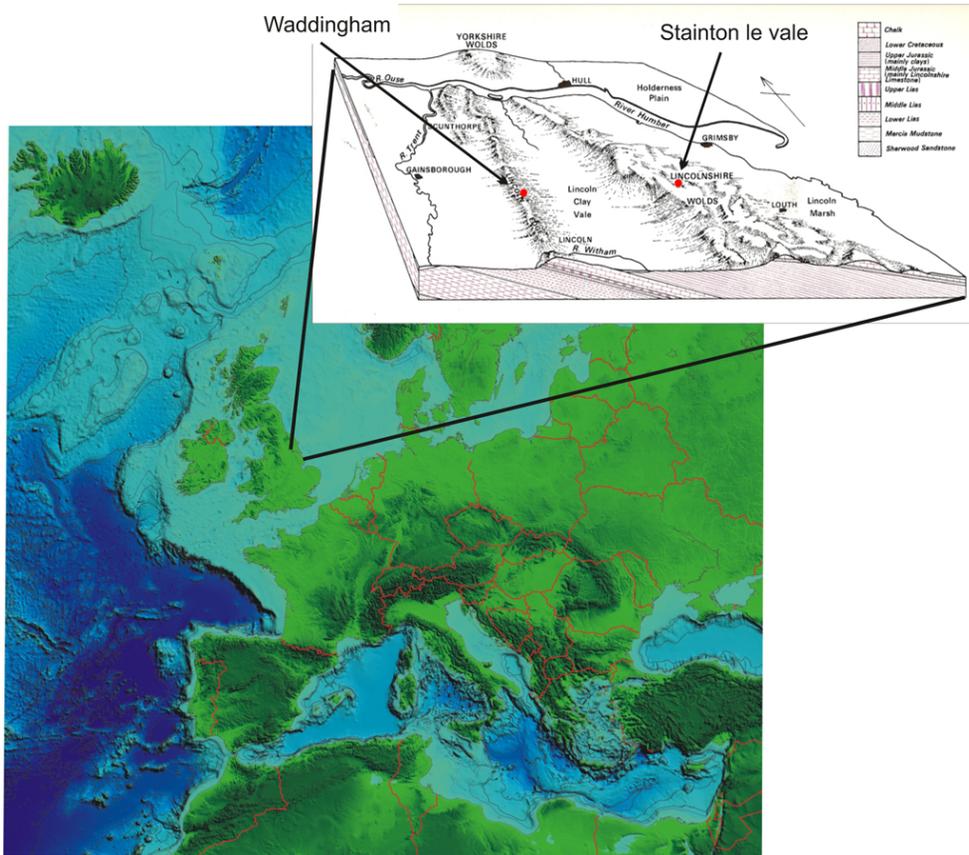


Fig. 10. Location of tufa and sub-tufa sites in Lincolnshire, UK. Insert geological map from (Kent et al., 1980).

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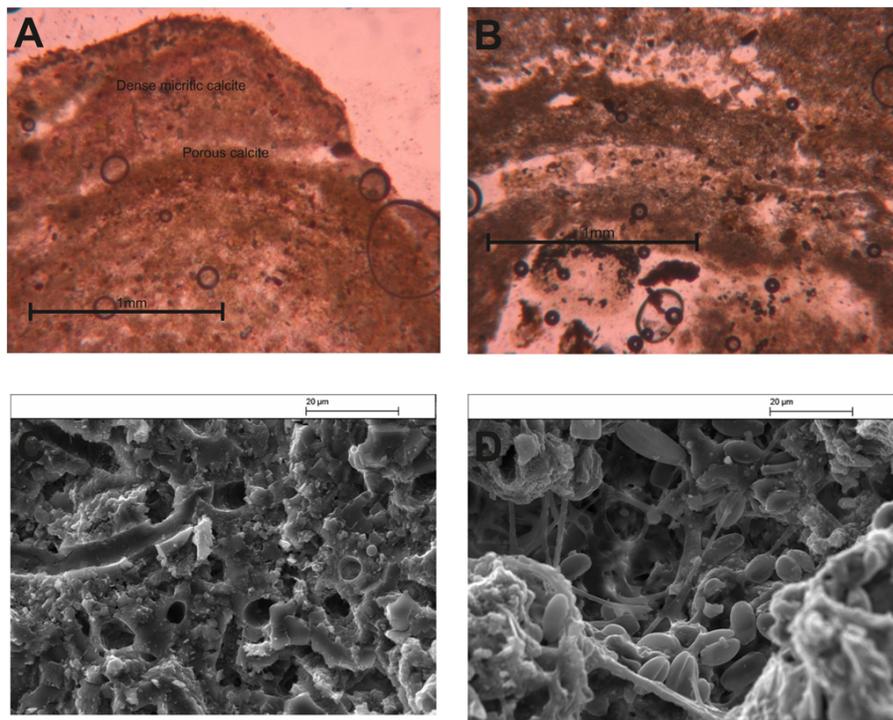


Fig. 11. Photomicrographs of tufa deposit from Stainton, Lincolnshire, UK. **(A and B)** transmitted light image showing alternative layers of micrite and porous calcite. **(C)** SEM image showing tubular holes in calcite left by loss of cyanobacterial filaments. **(D)** Clotted calcite bodies with cyanobacterial filaments and diatoms in the centre of the view.

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