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STATE OF THE SCIENCE

Decoding tufa and travertine (fresh water carbonates) in the sedimentary record: The state of the art

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ABSTRACT

Traditionally, fresh water carbonate research has focused on the sedimentology and palaeontology of ancient lacustrine deposits. Lithofacies in such low-energy deposits are typically fine-grained, developed uniformly in a generally concentric distribution ('bulls-eye' pattern) and are predictable even when preserved imperfectly. In contrast, because of their local lithofacies and palaeontological complexities, fluvial carbonates were either delegated to a status of 'minor geomorphological features' or barely considered prior to the 1970s. This viewpoint was based on the depositional record of fluvial and spring-fed fresh water carbonates, which were considered to be restricted generally to localized karstic areas. Such deposits are often preserved as scattered patches of ambient temperature tufa. Occasionally, however, in active tectonic areas, localized travertine deposits are also developed from deeply circulating hydrothermal waters. With a few exceptions (for example, basins with high subsidence rates or in arid climate zones), these fresh water carbonates are prone to erosion from continuing river incision and thus may not be preserved in the geological record. A partial record of fluvial and spring-deposited carbonates is often preserved in Quaternary deposits, but the record in older deposits is typically fragmentary and often diagenetically modified. Yet once their unique facies architecture (and specialized nomenclature) is understood, these carbonates provide an important record of past sedimentological cycles of great value in palaeoenvironmental landscape modelling. The emphasis of modern research is to acquire information that explains how active systems function. In this respect, tufas reveal much of how carbonate precipitation is a shared product of physico-chemical and microbiological biomediation processes. Likewise, travertines not only show an intimate interrelation with active tectonism but also hold great potential as monitors of past volcanic carbon dioxide emissions. In addition, both tufas and travertines contain palynological records that can be used as proxy indicators of climate change. Perhaps no other field of sedimentology has witnessed more developments and applications over such a brief period of study.

Keywords Calcareous tufa, fresh water carbonate, sedimentology, terrestrial carbonate, travertine.

INTRODUCTION

Terrestrial carbonates comprise a wide spectrum of lithologies (speleothems, calcrete, lacustrine limestone, travertines and tufas) which are mainly precipitated under subaerial conditions from calcium bicarbonate-rich waters in a large variety of depositional and diagenetic settings. These carbonates are characterized by a distinct range of lithological, petrological and geochemical properties which clearly distinguish them from their marine counterparts. Over the past 20 years, they have risen in status from minor curiosities to a major new research frontier. This interest derives first from their widespread distribution in continental settings, and second because they have long been recognized as important repositories of proxy-palaeoenvironmental information. This has presented a spectrum of opportunities ranging from the reconstruction of past ecosystems and environments to analyses of tectonic and sedimentary regimes. Recent developments in analytical techniques have also shown that it is possible to use travertine and tufa in several new, unexpected ways that relate to elemental biomediation processes, bioremediation, palaeoenvironmental markers, proxies for interpreting climate change and even proxies for extraterrestrial life. The present review aims to provide a concise summary of the general aspects of travertine and tufa, including classification, morphology and geochemistry, with a focus on their main applications in past, present and future research.

TRAVERTINE AND TUFA: A CONTROVERSIAL NOMENCLATURE

The terms tufa and travertine are often used indiscriminately as alternative names for the same fresh water limestone material (Julià, 1983). In particular, the term 'travertine' has been overused as a descriptive term for all crystalline varieties of fresh water carbonate. Others have distinguished powdery whitish tufa or calc tufa varieties. The terms tufa and travertine have also been applied indiscriminately to cave deposits (see Pentecost, 1981). Others (Irion & Müller, 1968) use the term calc sinter as a term for fresh water carbonates. Pentecost & Viles (1994) and Viles & Goudie (1990) presented a range of other terms and classifications, many of which lack precision.

Several recent articles have focused upon genetic definitions, based upon, for example, water temperature, source of carbon dioxide (Pedley, 1990; Pentecost & Viles, 1994; Jones & Renaut, 2010) or upon the chemical mechanism involved in precipitation (Pentecost, 2005). Thus, 'travertine' has been reserved by many authors as a term for warm to hot water hydrothermal precipitates whereas 'tufa' has been reserved for ambient temperature (cool water) deposits (Pedley, 1990). For temperature-based definitions, water temperatures have been measured directly in active depositing sites, or estimated indirectly from associated organisms and fossils (Pedley, 1990; Koban & Schweigert, 1993).

Definitions of cool water tufa frequently refer to, or even require, the presence of macrophytes in addition to cyanobacteria, heterotrophic bacteria and algae, the suggestion being that temperatures must remain below 30°C for these organisms to survive. However, Pentecost *et al.* (2003) discussed the difficulties in defining what constituted a 'hot' spring in ancient deposits, while Brasier (2011) reiterated how the terms 'tufa' and 'travertine', which imply circumstances that cannot be verified easily in 'deep time', might be avoided in favour of more descriptive terminology.

Without doubt, a water temperature classification as an indicator of shallow versus deep-circulating ground waters (and consequently of travertine or tufa) is oversimplified. In fact, low-temperature fresh water carbonates, such as the Chinese deposits of Huanglong [10° at 3500 m above sea-level (asl); Zhang *et al.*, 2012] and of Baishuitai (7° at 3000 m asl; Liu *et al.*, 2010), might easily be attributed to travertines due to their geochemical characteristics. Interestingly, Keppel *et al.* (2011) described typical phytohermal framestone tufa deposited from 20 to 27°C waters and interpreted them as super-ambient temperature meteogene ground water in origin, based on the lack of significant chemical or temperature variance between samples collected at different times of the year.

When analysing travertine and tufa, an integrated approach is critical to understanding and accurately interpreting the depositional environment. The textures, the mineralogy and the geochemistry of the fossil deposits, the associated biota and the chemistry of the waters from which they formed, as well as the likely geomorphological, hydrological and tectonic settings in which the carbonates were deposited must be considered. In addition, the identification of a clear modern analogue is needed in order to understand the processes and controls operating in these settings and also to better understand their significance in the fill and evolution of continental basins (Table 1).

For this reason, the term travertine must be retained for continental carbonates mainly composed of calcium carbonate deposits produced from non-marine, supersaturated calcium bicarbonate-rich waters, typically hydrothermal in origin. Travertine deposits are characterized chiefly by high depositional rates, regular bedding

Table 1. Main distinctive characteristics of travertine and tufa (numerical data mainly derived from Pentecost, 2005; Gandin & Capezzuoli, 2008 and references therein).

	Travertine	Tufa
Depositional processes	Dominantly abiotic	Dominantly biotic
HCO_3^- content (mmol/l)	>7	<6
$\delta^{13}C$ (PDB‰)	−1 to +10	<0
DIC (mmol/l)	>10	<8
Water temperature	Thermal, generally higher than 30°C	Ambient, generally lower than 20°C
Mineralogy	Calcite, aragonite	Calcite
Depositional rate	Higher (cm to m/year)	Lower (mm to cm/year)
Fabric	Mainly regularly bedded to fine laminated	Mainly poorly bedded
Crystal calcite size	Macro (dendritic, bladed or acicular) to micritic crystals	Dominantly micritic to microsparitic crystals
Primary porosity	Generally low (less than 30%)	Generally high (over 40%)
Biological content	Low (bacteria and cyanophytes)	Very high (micro to macrophytes)
Depositional morphologies	Multi-symmetrical bodies (mounds, ridges and slopes)	Axial-symmetrical bodies (cascade, dams and barrages)
Distinctive lithofacies	Coated bubbles, shrubs	Phytoherms
Hydrological setting	Regular, generally permanent flow	Variable, rainfall-dependent flow
Climatic control on deposition	Less dependent	Strictly dependent
Anthropogenic influence on deposition	Scarcely influenced	Deeply influenced
Tectonic relation	Always present	Often absent

and fine lamination, low porosity, low permeability and an inorganic crystalline fabric. Bacteria and cyanophytes typically are the only associated organic constituents, due to the presence of unsuitable factors (for example, high temperature, high rates of deposition, pH and sulphur) for plant and tree growth (macrophytes). Aragonite rather than calcite may also be present and $\delta^{13}C$ is typically high (positive or slightly negative). Such deposits are typical of tectonically active areas where geothermal heat flux (endogenic or volcanic) is high.

In contrast, the term tufa (Ford & Pedley, 1996; Pedley, 2009) refers to continental carbonates, composed dominantly of calcite and typical of karstic areas. These are typically produced from ambient temperature, calcium bicarbonate-rich waters which are characterized by relatively low depositional rates producing highly porous bodies with poor bedding and lenticular profiles, but containing abundant remains of microphytes and macrophytes, invertebrates and bacteria. Secondary carbonate deposits (cements and speleothems) may also be associated. Aragonite is usually absent (except from peculiar high Mg/Ca ratio spring waters; Owen *et al.*, 2010) and $\delta^{13}C$ is always low (very negative).

The distinction between these two lithotype associations is not always clear since some cool water deposits can represent a lateral development of cooled thermal waters. In fact, macrovegetation readily colonizes the cooler water areas downstream from hydrothermal resurgence points. Confusion in the field is mainly encountered where tufa and travertine are interlayered, such as in distal areas of travertine flowstones which have cooled sufficiently to permit colonization by microphytes and macrophytes (Ford & Pedley, 1996; Evans, 1999; Capezzuoli *et al.*, 2008; Brogi *et al.*, 2012). However, the sedimentary facies and geometry of these tufa deposits in the field and their incidental juxtaposition with typical travertine facies, are sufficient, in most cases, to suggest the primary physical characteristics of the water source. Consequently, it is generally possible on field evidence alone, even in ancient deposits, to make a clear distinction between travertines and tufas and to distinguish the origin of their water source (Pedley, 2009). However, there are a group of tufas characterized by a typical hydrochemical signature indicative of ambient temperature precipitation from cooled, deeply cycled (geothermal) waters that are more difficult to interpret; they are generally encountered in the peripheral sectors of geothermal regions with a recently active tectonic history (for example, Italy). The term 'travitufa' is suggested in order to distinguish them from normal tufas.

SEDIMENTARY FACIES

Despite growing interest, the classification of travertine and tufa facies has presented many problems due to the number of parameters that influence the final depositional product (for example, chemistry, hydrology, morphology, microbiology and botany), and no clear classification scheme embracing both tufas and travertines has yet been proposed. However, classification schemes based on facies types typical of cold, warm and hot water systems have been designed to facilitate identification and discussion. Hence, different schemes use different criteria related to petrography, morphology, deposition rate, climate, geochemistry, etc. (Zamarreño *et al.*, 1997; Guo & Riding, 1998; Fouke *et al.*, 2000; Carthew *et al.*, 2003; Gandin & Capezzuoli, 2008). Details of the basin-scale processes at the time of deposition, however, are often masked or even lost by later continental erosion, and the remaining fragments are frequently insufficient to provide a full interpretation of depositional scenarios.

DEPOSITIONAL ENVIRONMENTS AND MORPHOLOGIES

In contrast with most continental deposits, terrestrial carbonates are capable of constructing rapidly lithified rocks with positive relief at the time of deposition. The abiotic/bio-induced build-up process is responsible for their rapid depositional rate. In tufa, for instance, depositional rates have been calculated in fossil and active deposits by several authors, ranging from 0·32 mm/year (Heiman & Sass, 1989), 0·8 mm/year (Peña *et al.*, 2000), 1·2 to 2·4 mm/year (Andrews *et al.*, 2000) and 42 mm/year (Weijermars *et al.*, 1986). For a more detailed review, see Gradzinski (2010) and Vàzquez-Urbez *et al.* (2010a). Travertine depositional rates can be even higher. Comparatively few measurements have been made but most attest to the rapid accumulation of travertines. The data range between 1 mm/year and 1000 mm/year with a mean of around 200 mm/year (Pentecost, 2005). Consequently, even if fresh water carbonate events are of short duration in the geological record (Ford & Pedley, 1996), travertine and tufa are capable of rapidly transforming the landscape and may have a major influence on its evolution.

Perhaps the most common manifestation of fresh water carbonate deposition is the terrace. Such surfaces may be inclined gently and cover several square kilometres, as in the case of geothermal hot spring sites. Tufa terraces may be composed of tens of kilometres of near horizontal sheets comprised of lacustrine, paludal and barrage lithofacies; their modern distribution from the tropics to the Arctic confirms their significance in the continental geomorphological record, and illustrates the importance of better understanding depositional processes rooted in fluid dynamics, precipitation kinetics and crystal growth dynamics (Goldenfeld *et al.*, 2006; Hammer *et al.*, 2010).

Nonetheless, physico-chemical ground water parameters and external biotic–abiotic mechanisms directly determine peculiar travertine and tufa morphotypes and these deserve detailed consideration. In particular, microbial composition, associated vegetation type, substrate topography and fluvial and ground water hydrochemistry contribute significantly to depositional style and preservation potential. All of these factors influence the final carbonate morphology and provide criteria for their classification (Table 1).

Travertine

Depositional and morphological classifications have been proposed by several authors (Altunel & Hancock, 1993b; Guo & Riding, 1998; Fouke *et al.*, 2000; Veysey *et al.*, 2008; Guido *et al.*, 2010; Guido & Campbell, 2011, 2012). Many travertines are associated with fissures which vent hot, deeply circulated waters to the surface.

Vent environments (proximal)

Travertine deposits are focused frequently around discrete springs associated with convective hydrothermal systems, often under high pressure, and enhanced by bedrock damage that give rise to connected fractures and enhanced permeabilities in the bed rock. Such scenarios favour circulation and upwelling of hydrothermal fluids (Rowland & Sibson, 2004). Precipitation events are triggered frequently by CO_2 pressure fluctuations (Uysal *et al.*, 2009) and seismic activity (Becken *et al.*, 2011). The shallow plumbing system, representing conduits for the upwelling thermal water, is lined by variably shaped calcite/aragonite crystals (sparitic, acicular, dendritic and platy) developed into non-porous, sub-vertical crystalline laminated crusts (banded travertine: Altunel & Hancock, 1993a,b, 1996; Uysal *et al.*, 2007, 2009, 2011). These sheets are best developed in the throat of the travertine vent system but commonly also extend laterally into injection veins and sill-like structures (De Filippis *et al.*, 2012), and decrease in thickness and frequency away from the vent conduits.

At the water surface, travertine rapidly deposits and quickly develops into steep-sided constructional morphologies. If this occurs in an unusual subaqueous setting (travertine pipes and pinnacles, Hillaire-Marcel *et al.*, 1986; Hillaire-Marcel & Casanova, 1987), the resulting macrofacies are more porous and are connected intimately with algal-microbial interactions. In contrast, their more commonly encountered epigean counterparts generally consist of finely laminated drapes often composed of macrocrystalline precipitates deposited from thin, laminar flowing sheets of rapidly cooling water. Depending on the chemical and physical characteristics of these thermal waters, irregular masses of filamentous bacteria may locally colonize pool and channel margins in the vicinity of the vent (Fouke *et al.*, 2000; Takashima & Kano, 2008; Di Benedetto *et al.*, 2011; Fouke, 2011). Here, they are often associated with microsparitic to micritic laminae which may build up into small (millimetre to centimetre scale) shrubby growths, especially in shallow pools. Ultimately, ledges can develop along the pool margins and larger domes may form around vent resurgence points. These carbonates are characterized by a vast array of crystal forms, from coarse dendritic to platy and spherulitic calcite (Jones & Renaut, 1996, 1998, 2010).

The resulting macro-morphologies are represented by two end member types: circular mounds and linear-to-arcuate fissure ridges. As discussed by several authors (Curewitz & Karson, 1997; Brogi & Capezzuoli, 2009), development of each type is driven by substrate competence and permeability. For example, travertine fissure-ridges mainly develop on brittle-fracturing bedrock exposed at the surface, while isolated thermal springs, such as towers, pinnacles and mounds, generally form on unconsolidated sediments (Hancock *et al.*, 1999; Brogi & Capezzuoli, 2009) and are often point sourced (Fig. 1).

Slope environments (intermediate)

Thermal waters flowing away from the resurgence area rapidly cool and degas. As temperature falls, the environment is more conducive to bacterial colonization and a more varied range of precipitates often develop. Altunel & Hancock (1993b) distinguished two kinds of depositional systems (terrace and range-front sheets) in the Pamukkale deposits (Turkey). Their morphologies are controlled by the underlying morphology being either gently inclined slope deposits or steep slopes around graben fault margins.

Guo & Riding (1998) suggested an alternative classification using a depositional systems approach developed for the Rapolano Terme deposits of Italy. The final shape of the travertine slope system is controlled in the short-term by underlying morphology but high deposition rates rapidly bury it. This process leads to the deposition of variably inclined lobate bodies characterized by smooth to well-developed terraced slopes in their frontal part (Chafetz & Folk, 1984; Guo & Riding, 1998). Waters generally flow over the entire terrace surface in laminar sheets. Interactions between the pre-existing and evolving morphology, flow velocity and the biological components lead to deposition of a diverse range of travertine lithofacies (for example, crystalline crust, shrubs, coated bubbles and paper thin-rafts).

If discharge fluctuates, portions of the surface can become exposed to sub-aerial conditions and, depending on the period of exposure, may become partially cracked or pedogenically altered (autobrecciated sheets and more mature palaeosol horizons). When the free flow of thermal water becomes confined, rapid vertical travertine accretion occurs along the channel margins. Here, turbulent flow causes physico-chemical degassing (calc levée precipitation along the channel margins and accreting laminar sheet deposition along the channel base). This degassing rapidly leads to the vertical growth of

Fig. 1. Examples of travertine vent morphologies: (A) linear fissure ridge (Kamara ridge, Turkey), *ca* 40 m long; (B) linear ridge (*ca* 20 m long) formed by coalescent, aligned cone vents (Terme San Giovanni, Rapolano Terme, Italy); (C) high relief, circular mound (Castel di Luco, Italy - the mound is *ca* 10 m high); (D) low relief, circular mound with bubbling pool (Bullicame Spring, Viterbo, Italy - the pool is *ca* 7 m wide); (E) unusual mound at a triple fault junction (Cambazli, Turkey).

elevated, low sinuosity channels which may stand metres higher than the surrounding terrace and be hundreds of metres long ('self-built channels', Altunel & Hancock, 1993b; or 'catwalks', Violante *et al*., 1994).

Distal environments

Distal environments encompass all of the deposits forming in low relief topography from near-ambient water temperatures where hot ground water has been mixed with surface rain water. These settings, marshes (Guo & Riding, 1998), shallow lakes (Sant'Anna *et al*., 2004) or alluvial plains (Brogi *et al*., 2012), are typically transitional environments where travertine fabrics grade imperceptibly into tufa fabrics and biotic controls on depositional processes progressively increase (Rainey & Jones, 2009). Deposits are often dominated by lithoclastic material (often hillwash breccia), but coated grains, *in situ* coated macrophyte stems and subordinate, massive bedded layers of clotted peloidal micrite may develop. Many of these deposits could be classified as travitufa deposits.

Tufa

The classification of tufa into depositional models has been considered by several authors (Pedley, 1990, 2009; Violante *et al*., 1994; Ford & Pedley, 1996; Carthew *et al*., 2003, 2006). Classification is generally based on depositional geometry, details within sedimentary profiles and petrology (for example, perched springline, cascade, fluvial, lacustrine and paludal). In contrast, Arenas-Abad *et al*. (2010) reviewed previous schemes and selectively analysed their vertical facies successions as representing the sedimentary processes leading to their development. This analysis resulted in the grouping of all previously recognized fresh water carbonate facies into two process-related models: (i) low-gradient, non-stepped fluvial and fluvio-lacustrine conditions, generally with extensive development of oncoid and paludal facies; and (ii) high-gradient and stepped fluvial conditions typically with laminated fluvial and lacustrine facies and variable developments of barrages, waterfalls and dammed areas.

Resurgence environments (proximal)

Physico-chemical deposition of terrestrial carbonates is always associated with calcite crystal growth from CO_2-rich ground waters oversaturated in calcium ions. As water flows away from the resurgence point, carbon dioxide escapes into the atmosphere and tips the increasingly supersaturated solution in favour of calcite precipitation. However, calcite precipitated from microbial biomediation is increasingly recognized as important (Rogerson *et al.*, 2008; Pedley *et al.*, 2009). This contribution is considerably greater in tufa systems than in travertine systems because biofilms are able to biomediate calcite internally even where surrounding waters are insufficiently saturated for abiotic calcite precipitation. The combined result of the two processes effectively strips calcite from the fluvial system quite proximal to the source; hence, it is possible to recognize the inputs of multiple resurgences within a single river course.

These processes may cause tufa deposition near a single subaerial resurgence point (for example, perched springline, Pedley, 1990; mound springs, Keppel *et al.*, 2011) and the deposit may be composed predominantly of highly irregular, very porous macrobiota dominated, depositional fabrics (phytohermal facies). Alternatively, tufa may develop at multiple resurgence sites along a watercourse to produce barrage tufas (Pedley *et al.*, 1996; Pentecost, 2005). On steep subaerial slopes, point sourced resurgences are invariably associated with lobate perched springline tufas (Pedley *et al.*, 2003), whereas valley bottom and artesian resurgences lead to the development of spring mounds with lower width to height ratios than are found in lacustrine settings (Pedley & Hill, 2002).

Less commonly, tufas may develop at lake floor resurgences within fresh water, hyposaline or hypersaline water bodies (Kempe *et al.*, 1991; Larsen, 1994; Rosen *et al.*, 2004; Jones & Renaut, 2010; Guo & Chafetz, 2012). In these subaqueous situations, porous stromatolitic/thrombolitic build ups are more usual and may give rise to mound morphologies.

Intermediate environments

Intermediate environments cover those parts of fluvial systems located considerable distances from resurgences. Waters here are generally undersaturated; consequently, little carbonate precipitation is to be expected. However, other mechanisms encouraging precipitation within a river system include evaporation within ponded areas and extensive colonization both by biofilms and aquatic vegetation (Perri *et al.*, 2011; Manzo *et al.*, 2012). In addition, morphological steps along water courses also cause enhanced turbulence and lead to further release of carbon dioxide, thereby encouraging physico-chemical precipitation. Small cascades and barrages are the most representative morphotypes (for example, Plitvice Jezero and Krka River barrages – Croatia; Emeis *et al.*, 1987; Lojen *et al.*, 2004; Fig. 2). Unfortunately, it is often difficult to distinguish barrages forming adjacent to resurgences from those developed at morphological thalweg steps where physico-chemical processes are more active.

Upstream areas of these cascades and barrages are often characterized by low-energy/stagnant water settings (paludinal marshes, ponds or small lakes). Planktonic bacteria and algae abound in these low energy, pool settings and there is often a tendency, especially during the summer months, for whitings to develop (Thompson *et al.*, 1997; Ohlendorf & Sturm, 2001; Dittrich *et al.*, 2004). These whitings are caused by planktonic microbial metabolic process triggered precipitation of minimicrite crystallites, and contribute considerable volumes of lime mud to the pool floor. Evaporation also concentrates cations close to the air–water interface, further enhancing the carbonate precipitation process. Extensive biofilm colonization of marginal aquatic vegetation is also capable of encouraging thin laminar carbonate precipitation on detrital nuclei (superficial oncoids) and semi-aquatic macrophytes (cylindrical oncoids) in intermediate environments.

Distal environments

In the downflow direction, waters progressively lose their dissolved calcium carbonate and their capacity to deposit calcite is reduced or stopped. In distal riverine environments, detrital tufa deposition dominates but may become progressively diluted with other clastic input (Ortiz *et al.*, 2009; Capezzuoli *et al.*, 2010). Where present, detrital tufas typically are developed

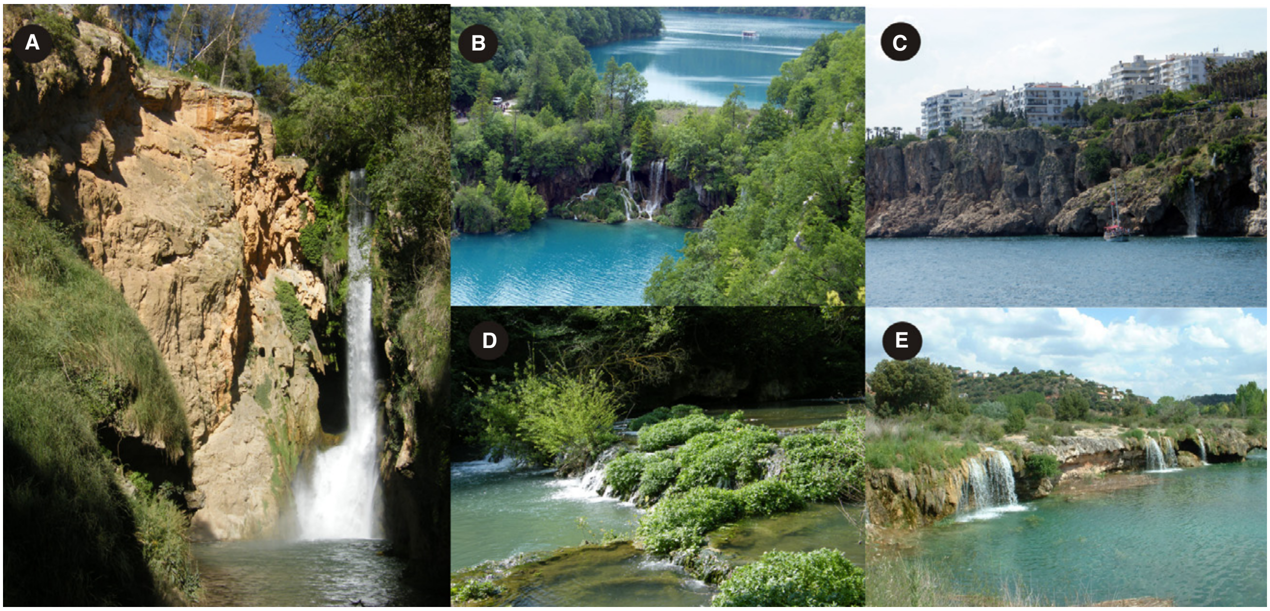

Fig. 2. Examples of tufa morphologies: (A) cascade (*ca* 50 m high) at Monastiero de Piedra Natural Park (Zaragoza – Spain); (B) lakes and cascade (*ca* 15 m high) at Plitvice Jezera (Croatia); (C) fossil tufa cliff (*ca* 20 m high) at Antalya (Turkey); (D) small barrages (*ca* 50 cm high) at Diborra Gorge (Siena, Italy); (E) small cascades (*ca* 2 m high) below Lagunas Redondilla, Ruidera Pools Natural Park (Spain).

into braidplain valley fills. In profile, the deposits show interpenetrative channelling, small-scale channel bar structures and occasional ripple bedforms. Deposits typically are well-sorted but grade rapidly downstream into finer particles because individual tufa clasts are easily abraded, especially if there is a siliciclastic component present. Where rivers enter lakes, small detrital tufa deltas may form and medium to fine calciturbidite couplet sheets may develop peripherally towards the depocentres. Many such lakes, especially in relatively cool and humid climates, are well-stratified meromictic waterbodies (for a modern definition see Walker & Likens, 1975; Hakala, 2004). In these stratified waterbodies, the monimolimnion may remain undisturbed for decades to centuries. These sites slowly accumulate detrital organics which survive as sapropel layers in the neutral to acidic waters below the chemocline (Pedley, 1993). By contrast, in warmer climates, when the sedimentation rate is not too high, organics generally decompose or oxidize too rapidly for sapropel accumulation to occur (Pedley *et al.*, 1996) and holomictic lakes are more typical. In arid climates evaporation within the lake, with or without the planktonic algal contribution may give rise to micrite precipitation and deposition of lacustrine limestone (Gierlowski-Kordesch, 2010).

Tufa versus travertine and internal drainage basins

Caution should be exercised when classifying lacustrine mound and marginal carbonates in areas of geothermal activity (for example, Western USA hypersaline lakes, Scholl, 1960; Guo & Chafetz, 2012; Northern Greece, Hancock *et al.*, 1999; Inner Mongolia, Arp *et al.*, 1998; Eastern Africa, Renaut *et al.*, 2013). Some of these precipitates, whether physico-chemical or microbial, are the product of carbonate precipitation from springs issuing into lakes at temperatures of more than 30° (and up to 90°) centigrade (for example, Pyramid Lake, Arp *et al.*, 1999; Mono Lake, Dunn, 1953; Lake Bogoria, Renaut *et al.*, 2013). The clear implication here is that the lake waters are derived from multiple origins which have been modified by meteoric and geothermal sourcing and by evaporation. Consequently, the derived elemental and isotope signatures of any carbonate precipitates (for example, mounds and pinnacles) developed either proximal to the hydrothermal vents or distally around the ambient temperature lake margins (for example, microherms) are likely to be complex. Those precipitates formed at the lake-geothermal spring interface will have characteristics closely comparable with travertines *sensu stricto*. Importantly, however, hot spring waters will mix rapidly into the surrounding lake waters and ambient temperature carbonate fabrics more akin to tufas often form. Around lake margins stromatolite laminites, thrombolites and even phytoherms are frequently established. Nevertheless, the host fluids from which they precipitated will not be fresh water. The carbonate deposits will show variable chemical and isotopic characteristics set at the time of precipitation by the degree of lake desiccation, and the relative inputs of meteoric and geothermal waters. Consequently, whether physico-chemical or biomediated, the deposits merit their own specific designation. In order to avoid confusion, it is suggested that any carbonate precipitated under playa lake conditions where resurgent waters are geothermal should be designated as a 'saline travertine'. Precipitates within playa lakes where waters are at ambient temperatures and derived from meteoric or mixed sources should be designated as a 'saline tufa'. Many of the saline lakes containing these precipitates are shallow and lie in tectonically active areas (for example, Lake Bogoria; Renaut *et al.*, 2013). Such sites may show characteristics similar to fresh water, meteoric dominated precipitate phases during lake highstands, and both hypersaline, geothermal dominated precipitate phases and true travertines during lowstands; these may also be intercalated with evaporites.

NEW PERSPECTIVES

Thirty years after the carbonate petrological characterizations of Chafetz & Folk (1984), travertines and tufas provide a new frontier for future carbonate research. Innovative new research fields are now pushing the frontiers back and revealing unexpected clues, not only to crystal precipitation and early diagenetic processes, but also to past climatic, tectonic and hydrological regimes and even to the origins of life.

Geomicrobiology in tufa and travertine

Geomicrobiology concerns the role of microbes and microbial processes in geological and geochemical processes and vice versa. The application of geomicrobial processes, especially to the cool water carbonate precipitation process, has already been discussed briefly here. Current research is now investigating biofilm microstructure and ultrastructure and the intercellular processes leading to carbonate bioprecipitation (see Pedley, 2013). In particular, Turner & Jones (2005) and Pedley *et al.* (2009) have demonstrated the close control on skeletal crystal triad precipitation by microbial filaments. Pedley *et al.* (2009) have highlighted the precipitation of 'Swiss cheese' microspar crystals and nanospheres within living fresh water prokaryote-microphyte tufa biofilms.

The field has seen enormous advances in the past three decades fundamentally changing the understanding of how microbial life impacts the Earth. This change is nowhere more so than in the study of extremophile organisms, the microorganisms that thrive in environments normally considered hostile (Konhauser, 2009). Such locations may include extremely hot (hot springs or mid-ocean ridge black smokers) environments (Kerr & Turner, 1996), extremely saline environments, or even extraterrestrial environments.

Palaeontologists and biologists now employ travertine deposits as analogue settings for early life on Earth (Fig. 3; Walter & Des Marais, 1993; Farmer, 2000; Riding, 2000; Fouke *et al.*, 2000; Fouke, 2011). By analogy to Earth, specialized microbes may have also existed in the heated, mineralized waters of extraterrestrial bodies. Thermal deposits on Earth can rapidly entomb individual organisms and even complete ecosystems within spring-deposited minerals (Norris & Castenholz, 2006). These often record physico-chemical signatures of the original habitat (Cady & Farmer, 1996; Trewin & Rice, 2004; Guido *et al.*, 2010). Since the geological relations which produce hot springs can be recognized in extraterrestrial orbital imagery, directed searches for microfossils in such deposits are deemed possible. For this reason, hot spring deposits have been cited as prime locations for exobiological exploration (NASA, 1995). This explanation is due to the fact that a fossil hot spring deposit on a desiccated extraterrestrial surface might reveal evidence of biological weathering, or preserve textures such as nanospheres (Jones & Peng, 2012) and 'crystal shrubs' (Chafetz & Guidry, 1999) that have been attributed on Earth to biomineralization. This is a possibility on Mars, where an active subsurface spring might still nurture microorganisms adapted to dark, anaerobic conditions. In any case, a Martian hot spring would be a prime site in the search for past or present extraterrestrial life (Allen *et al.*, 2000; Allen & Oehler, 2008).

Fig. 3. Diverse (in colour) microbial communities and changes in their relative lateral position between thermophyllic and photosynthesizing bacteria in several thermal systems. Examples from: (A) Egerszalok (Hungary; 60°C - the channels are *ca* 10 m long); (B) Bagni San Filippo (Italy; 52°C - the pool is *ca* 2 m long); (C) Karahayt (Turkey; 58°C - the thermal system is *ca* 4 m high); and (D) Castelnuovo Berardenga (Italy; 39°C - the pool is *ca* 10 m long).

Neotectonics and geothermal implications

The intimate connection between travertine and active tectonics is a basic concept in neotectonic and seismological studies, because the location of travertine deposits is a very useful tool for identifying active and potentially hazardous faults. In some cases, travertine masses can also reveal much about palaeoseismology (Sibson, 1987; Muir-Wood, 1993; Martinez-Diaz & Hernandez-Enrile, 2001; Piper *et al.*, 2007; Nishikawa *et al.*, 2012), because of their potential for accurate dating. Improved knowledge of the palaeo-seismic history of faults using the U-series dating technique provides valuable additional data with which to constrain and improve simulations of earthquake fault system dynamics (Uysal *et al.*, 2007; Brogi *et al.*, 2010a).

The term 'Travitonics' emphasizes the close relation between travertine deposition and tectonics (Hancock *et al.*, 1999). Travertines are considered to be important tools for tectonic investigations due to the fact that the fracture network typifying the fault damage zones plays an important role in the circulation and upwelling of hydrothermal fluids in geothermal areas (Barbier, 2002). For this reason, travertine masses deposited from thermal springs are considered good indicators of tectonic activity (Altunel & Hancock, 1993a,b; Hancock *et al.*, 1999; Altunel, 2005) and, consequently, a potential archive recording of the surface activity of deep fluid circulation in a geothermal reservoir (Minissale, 2004; Crossey *et al.*, 2006; Nelson *et al.*, 2009; Banerjee *et al.*, 2011).

Good examples of this interaction are illustrated by the Jurassic hot spring deposits of the Deseado Massif, Argentina (Guido & Campbell, 2009; Guido *et al.*, 2010). Where there is lateral evolution and cooling from thermal-derived fluids, some associated tufa deposits have been used as indicators of tectonic activity in Brazil (Corrêa *et al.*, 2011) and in Italy (Brogi *et al.*, 2012). Active hydrothermal-derived carbonate deposits represent some of the best surface manifestations of a deep-seated geothermal system, as they provide information on water reservoir temperature (Navarro *et al.*, 2011; Pasvanoğlu & Chandrasekharam, 2011) and of its sustainability (Fórizs *et al.*, 2011; Carucci *et al.*, 2012). Thermal water depositional temperatures are also obtainable from ancient travertine deposits by using the clumped-isotope thermometer method (Gosh *et al.*, 2006). Alternatively, when coupled with a $\delta^{18}O$ water composition estimate, palaeotemperatures can be obtained from the water–bicarbonate oxygen isotope equilibrium fractionation value (Halas & Wolacewicz, 1982, as an alternative to employing the water-travertine equilibrium fractionation of Friedman & O'Neil, 1977). Recent applications in Kele *et al.* (2008, 2011) show an 8 to 9°C difference with respect to previous palaeotemperature calculations.

Information about palaeoenvironmental conditions and the geothermal characteristics of the associated fluids are potentially available from fluid inclusion analyses of ancient travertine bodies. This method, mainly used for interpreting the genesis of metamorphic and volcanic rocks, has been applied in the study of Pleistocene travertine in Argentina (Antuco travertine; Gibert *et al.*, 2005) and in recent laminar deposits at Gordale, England and Bagno Vignoni, Italy (Parnell & Baron, 2004).

Volcanoes and CO_2 emissions

Travertine deposits and volcanism are often closely associated due to hot crustal-fluid flow, active tectonism and related surface hot springs (Crossey *et al.*, 2006). Carbon dioxide is a common magma constituent and during magma upwelling, pressure reduction leads to outgassing and eventual CO_2 release.

Circulating ground waters are capable of dissolving large quantities of gas under high hydrostatic pressures. The resulting solutions dissolve calcium carbonate at depth, providing highly concentrated bicarbonate solutions that commence degassing as the waters rise (Chiodini *et al.*, 1995; Frondini *et al.*, 2008).

In active tectonic regions with extensional regimes, this process may be encouraged by the presence of deep faults that act as preferential conduits for upwelling fluids. For example, Brogi *et al.* (2010b) investigated the kinematics of the geological structures related to active evolution of the Mt. Amiata volcano (Southern Tuscany, Italy) from the tectonic deformation and structural features affecting the local travertine deposits of Bagni San Filippo (Fig. 4).

Because of the relatively high solubility of carbon dioxide in water, the occurrence of gas emissions at the surface depends on the quantitative ratio of ground water volumes circulating in the sub-surface relative to the amount of gas arriving from depth. Large volcanic CO_2 outputs are very important in Earth history, due to the fact that they may strongly influence climate and contribute to the rapid passage from glacial to interglacial periods (Huybers & Langmuir, 2009). By contrast, Uysal *et al.* (2009) proposed a positive feedback between water availability (rainfall) and surface discharge of carbon dioxide. Studies on Turkish travertine deposits testify to host rock fracturing by seismic shaking caused by fluid overpressuring in geothermic

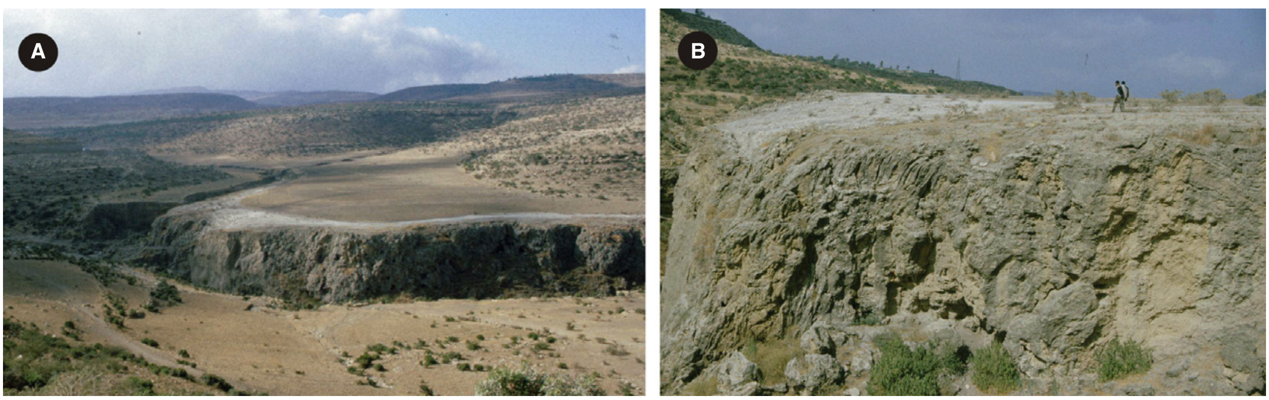

Fig. 4. (A) The Holocene perched springline tufa body of Mai-Makden (Ethiopia). The gorge is *ca* 10 m deep. (B) Detail of phytohermal framestones in the upper portion of its frontal part typifying a densely vegetated cascade environment very different from the present-day arid environment (man for scale, *ca* 1.8 m tall).

systems during dry climate periods. In this sense, climate variability controls the availability and quantity of geothermal waters, with relatively wet climate events leading to CO_2 discharge and dissipation at the surface, which may be associated with the deposition of terrace-mound travertines. In contrast, very dry climate events lead to CO_2 oversaturation in deep reservoirs and promote rapid exsolving and expansion of the dissolved gas leading to hydrothermal eruptions. Undoubtedly, the well-dated evolution of volcano-related travertine deposits offers the potential for deciphering links between ancient volcanism, active tectonism, hot crustal-fluid flow and the birth, growth and death of ancient hot springs (for example, Italian Mt. Etna area, D'Alessandro *et al.*, 2007; Argentinian San Agustìn deposit, Guido *et al.*, 2010).

Anthropogenic influence on natural environments

Tufa and travertine depositional environments provide favourable sites for human settlement activities (Gonzalez *et al.*, 2009). Consequently, they are often associated with hominid remains and traces of old civilizations (Kappelman *et al.*, 2008; Ashley *et al.*, 2010). Human influence on tufa deposition has been so profound during late historical times that deforestation, improved drainage and pollution are perceived as the most common causes for their depositional decline (Goudie *et al.*, 1993; Taylor *et al.*, 1998; Nyssen *et al.*, 2004). Recent case studies have documented a range of anthropogenic-associated environments including Plitvice lakes – Croatia (Horvatinčić *et al.*, 2006), coastal tufa of the Leeuwin-Naturaliste geographic region – Western Australia (Forbes *et al.*, 2010), Huanglong ravine and Xiangshui River – China (Liu *et al.*, 2011; Zhang *et al.*, 2012). In all cases, carbonate deposition rates have declined significantly as a result of phosphate pollution caused by tourism and agricultural activities within the catchment areas.

Landscape evolution

Fluvial deposits, and in particular the associated detrital deposits, commonly have a low preservation potential owing to the erosive effect of flowing waters. However, terraced, fluvial carbonate deposits appear to be a particularly promising tool for understanding the environmental and palaeohydrographical evolution of an area, since the morphology and depositional features of carbonate terraces are generally well-preserved by early lithification (Ordòñez *et al.*, 2005; Schulte *et al.*, 2008; Zentmyer *et al.*, 2008; Ortiz *et al.*, 2009; Capezzuoli *et al.*, 2010). Although outcrops are commonly poor, the internal architecture of terrace deposits can be revealed by ground-penetrating radar, especially in areas where the water table is low (Pedley *et al.*, 2000; McBride *et al.*, 2012). Using this method, Pedley *et al.* (2000) showed the former presence of an incised meandering limestone gorge below a tufa terrace and revealed details of a buried barrage-tufa succession. In a further example, within the Piedra River catchment (Spain), Vàzquez-Urbez *et al.* (2010b) distinguished two distinctly different episodes of fluvial activity which were triggered by a temporarily blocked river subsequent to tufa barrage aggradation within the primary river channel. In both episodes, channel avulsion diverted flow across a local divide and into a second water course.

The geomorphological evolution of a river valley can also reflect variations in palaeoclimate. Golubic (1969) recognized the cyclic nature of many deposits with each episode terminated by a deep erosive event probably triggered by environmental change. In particular, the downcutting of a series of terraces can often be directly related to tectonics or to major climate phases in the region. It has been noted that many rivers formed new terraces during warm periods or cold to warm transitions. In contrast, the rivers seem to have produced incised valleys following interglacial periods. These changes reflect responses driven by climate change, mainly at orbital (Milankovitch) frequencies (Bridgland & Westaway, 2008; Ortiz *et al.*, 2009).

The travertine terraced deposits along the Danube River (Hungary) are good examples of such interaction. Ruszkiczay-Rüdiger *et al.* (2005) conclude that they resulted from the emergence of the local mountain range during an epoch of significant climate changes and, as a consequence, periodic terrace carving, valley widening and terrace aggradation occurred.

Climate reconstruction

The importance of travertines and tufas for Quaternary studies derives primarily from their value as repositories of palaeoenvironmental data, much of which can be dated using radiometric techniques such as ^{14}C radiocarbon methods for Holocene–Late Pleistocene tufas

(Srdoč *et al.*, 1980, 1983) or uranium series ($^{230}Th/^{234}U$) and ($^{234}U/^{238}U$) methods for the older Quaternary (up to 400 ka and 1 Ma, respectively; Soligo *et al.*, 2002; Sierralta *et al.*, 2010; Brogi *et al.*, 2010a). Most reliable dates are obtained from autochthonous deposits such as back barrage pool deposits or stromatolitic crusts, but even these may possess contaminants in sufficient quantity to prevent reliable dating. Other isotopes may also be used ($^{228}Ra/^{226}Ra$, ^{210}Pb) but all of these methods are prone to error, caused by the presence of contaminants, recirculation or diagenesis (Schwarcz, 1990; Pentecost, 2005; Walker, 2005). Alternative techniques for dating of tufa and travertine deposits include thermoluminescence (Engin & Guven, 1997; Engin *et al.*, 1999) and electron spin resonance (ESR; Blackwell *et al.*, 2012).

Many studies emphasize the close relation between climate and tufa deposition (for reviews see: Pentecost, 2005; Andrews, 2006; Pedley, 2009), with tufas occurring more abundantly during humid and warm phases since they favour forest development and associated soil CO_2 production. This close relation further implies that, in dominantly humid and cold environments (for example, middle-northern latitudes), tufas may be used as proxies for warm interglacial phases (Griffiths & Pedley, 1995; Limondin-Lozouet *et al.*, 2010; Domínguez-Villar *et al.*, 2011). The former presence of active tufas in arid to semi-arid and temperate to tropical environments also testifies to important rainfall regime shifts in the geological record. This shift has been demonstrated in distal glacial transitional environments and for glacial periods (South Europe, Capezzuoli *et al.*, 2010; Alexandrowicz, 2012) and in semi-arid (Brazil, Auler & Smart, 2001; Spain, Luzón *et al.*, 2011) and desert settings (Namibia, Viles *et al.*, 2007; Libya, Cremaschi *et al.*, 2010; Ethiopia, Moeyersons *et al.*, 2006), where tufa deposits are a direct record of the wetter phases. Consequently, specifically in non-tectonically influenced settings, tufas are proxies for water availability and thereby vehicles for palaeohydrogeological studies. In contrast, the presence of tufas in tropical and monsoon-dominated settings testifies to an absence of destructive large wet season floods and, consequently, for reduced periods of rainfall (Carthew *et al.*, 2003, 2006; Fig. 5).

With regard to travertine deposition, many authors (Pentecost, 1995; Mesci *et al.*, 2008) emphasize the fact that the influence of climate on geothermal-related precipitation is generally less obvious. Nevertheless, Sturchio *et al.* (1994) for example, showed how travertine deposition in Wyoming was profoundly affected by Pleistocene glaciations. In that setting, prolonged freezing conditions prevented infiltration of water by blocking the hydrothermal circuit and modifying the hydraulic head. Such a circuit response could provide the perfect climate proxy. Climate change could also be registered within travertines by changes in $^{18}O/^{16}O$ ratios, while $^{13}C/^{12}C$ ratio shifts could highlight changes in the source of CO_2 with associated input on the Milankovitch cycles.

More realistically, travertines are linked to the availability of water, being influenced indirectly by tectonically driven ground water flow changes, which directly reflects rainfall availability and an elevated ground water table (Rihs *et al.*, 2000; Faccenna *et al.*, 2008; Zentmyer *et al.*, 2008). Geochemical studies and absolute dating of terrestrial carbonates in Central Italy (Minissale *et al.*, 2002) considered the effects of hydrogeology on ground water flow paths and resultant geochemistry. These studies concluded that travertines preserve a valuable record of palaeofluid composition and palaeoprecipitation.

In the same way, Liu *et al.* (2010) demonstrated, from studies of travertine deposits in south-west China, that rates of carbonate precipitation and the formation of lamination were controlled principally by rainfall. This may provide an additional approach for using ancient travertine deposits to reconstruct the climate in the past.

Macroflora and microflora

The analysis of palaeoenvironmental change using fresh water carbonate fossil faunas is possible because of the rich communities present in tufa, although this is less true for travertine (for a complete review see Pentecost, 2005). Fossil flora is mainly represented by macroremains (leaf impressions, fruits, moss cushions, twigs and seeds) and microremains (diatoms, pollens and algae). The analysis of these materials provides an important additional research strand that can be integrated with sedimentology for palaeoenvironmental analysis (for a complete review see Pentecost, 2005). Fresh water carbonate palynology has been applied less commonly because many still argue that pollen is poorly preserved in alkaline-dominated depositional environments (Traverse, 2007). Nevertheless, there are some notable successes, especially in Holocene ambient

Fig. 5. (A) Fissure ridge (*ca* 10 m long) at Bagni San Filippo (Italy). This travertine deposit is located at the tip zone of a strike-slip to oblique-slip fault along which eruptions of the Late Pleistocene volcano, Mount Amiata, occurred. Gas emissions and hot waters are issuing actively from this geothermal area, forming spectacular travertine bodies [the so-called 'White whale' slope travertine, *ca* 10 m high in (B)] and related macrocrystalline lithofacies [examples of thick crystalline crusts in (C)].

temperature tufa deposits (Burjachs & Julià, 1994; Taylor *et al.*, 1994, 1998; Vermoere *et al.*, 1999; Makhnach *et al.*, 2004; Pentecost, 2005; Schulte *et al.*, 2008; Currás *et al.*, 2012). Despite general misgivings, tufa carbonate palaeobotany is quite feasible and can provide valuable floral distribution data at local and regional scales, for palaeoclimatic reconstructions. In particular, vegetable macroremains from tufa deposits have contributed significantly to a better understanding of the evolution of modern European forest patterns, the past distribution of arboreal species (Ali *et al.*, 2003a,b; Fauvart *et al.*, 2012) and the effects of fire on the distribution of Holocene vegetation (Ali *et al.*, 2005a,b).

Work has barely commenced on the palynology of travertine deposits. Bertini *et al.* (2008) carried out palynological analyses in the Italian Rapolano and Tivoli sites, demonstrating that travertine deposits can also yield pollen in sufficient quantity to be of significant value in the investigation of late Quaternary palaeoclimates.

CONCLUSIONS

From humble beginnings, tufa and travertine research has developed internationally over three decades into a major field of carbonate sedimentology and palaeoenvironmental modelling. Tufa and travertine are continental carbonates that can be treated as part of a complex continuum of terrestrial deposits resulting from combined chemical and bio-induced precipitation processes. These extend from sub-terrestrial ground water sites (speleothems and calcretes), via subaerial fluvial sites (perched springlines and barrages) to perennially submerged continental depressions (paludal and lacustrine deposits). For these reasons, their classification must consider carefully the depositional setting and a number of extra-sedimentological parameters, including the associated physico-chemical and biotic elements (mineralogy and geochemistry, associated biota and chemistry of the depositing waters).

The term travertine should refer to calcium carbonate deposits produced from non-marine, supersaturated carbonate waters, typically hydrothermal in origin and chiefly marked by high depositional rates, regular, fine laminated bedding, with a dominantly inorganic crystalline fabric of low porosity and permeability. Microbial communities may be associated with this deposit; aragonite as well as calcite may be present and the $\delta^{13}C$ is typically high (positive or slightly negative).

In contrast, the term tufa should be applied to deposits consisting dominantly of calcite that are produced from low depositional rate, shallow cycled and karstic-derived, ambient temperature waters which are characterized by poorly bedded, highly porous fabrics. Microbiota and macrobiota are very common, and $\delta^{13}C$ is always low, while primary aragonite is typically absent except in spring waters with a high Mg/Ca ratio.

In the case of tufa fabrics precipitated from cooled thermal waters, the resulting deposits should be identified as 'travitufa'. These ambient temperature deposits are characterized by their deep-circulating hydrochemical signatures. Similarly, playa lakes (Salinas) contain peculiar carbonates that require special consideration. Those precipitated directly from thermal waters at the saline lake water-spring interface should be identified as 'saline travertines', whereas those derived from ambient temperature lake waters should be designated as 'saline tufas'. The strict application of these definitions makes the terms travertine and tufa useful indicators of specific hydrological and environmental conditions. For example, the 'tufa towers' mainly described from the Western USA Great Basin region (Scholl, 1960) and which closely resemble the 'travertine pipes' from the Eastern African rift lakes (Hillaire-Marcel *et al.*, 1986; Hillaire-Marcel & Casanova, 1987) would, on the basis of water geochemistry and tectonic-related characteristics, be described as saline travertines.

Consequently, the interpretation of depositional processes must be the initial procedure in tufa and travertine analysis and decoding. However, additional regional or global factors, such as biotic evolution, ground water circulation, global climate change and local to regional tectonic processes, must also be taken into consideration for their full interpretation. Consequently, a full understanding of these deposits necessitates a diverse, multidisciplinary approach.

Tufa and travertine research has played a pivotal role in the development of a number of novel research areas:

Fresh water Geomicrobiology: A new sub-discipline studying tufa and travertine generating biofilms and their role in the biomediation of calcium carbonate and their control on carbonate micro-fabrics.

'Travitonics': A new sub-discipline relating neotectonics and fracture controlled travertine development.

Fresh water Geochemistry: In particular, the study of volcanic CO_2 emissions and geothermal signatures preserved in travertine deposits.

Karst Geochemistry: The recognition and use of fresh water carbonates as important repositories of radiometric and stable isotope data in karstic regions.

Carbonate Geoarchaeology: A sub-discipline involved with the interaction of anthropogenic processes and carbonate environments.

Fresh water Carbonate Palynology: A new sub-discipline using fresh water carbonates as a proxy for the reconstruction of climate change in karst regions.

There are further fields yet to be revealed, which will undoubtedly shed considerable light on diagenetic processes in carbonates, including neodiagenesis (for example, the growth of nanospheres and microspar within biofilms, and related dissolution and precipitation processes) and subsequent fresh water diagenesis in the meteoric domain. The role of biofilms in the evolution of life on Earth is significant and may well have a direct bearing on the potential to develop and preserve extraterrestrial life. Finally, there are the potential economic aspects of these deposits which range from considerations of their value as building stones and sources of high grade calcium carbonate, to their potential as aquifers and recently as commercial hydrocarbon reservoirs (Wright, 2012).

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