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TRAVERTINE VERSUS CALCAREOUS TUFA: DISTINCTIVE PETROLOGIC FEATURES AND STABLE ISOTOPES SIGNATURES

Anna Gandin & Enrico Capezzuoli
Dip. Scienze della Terra, Università di Siena, Via Laterina 8, 53100 Siena
e.mail: gandin@unisi.it

Abstract: A. Gandin & E. Capezzuoli, *Travertine versus Calcareous tufa: distinctive petrologic features and stable isotopes signatures*. (IT ISSN 0394-3356, 2007).
Terrestrial limestones, mainly deposited as calcite crusts by carbonate-rich waters flowing in subaerial settings, originate from warm-to-hot waters of hydrothermal provenance (travertines) or from cool waters of karstic derivation (calcareous tufa). The two groups of concretionary carbonates are actively forming in different geomorphologic settings such as cool-water springs and fluvial valleys, or in the surroundings of the emergence of thermal springs. Fossil remains of these rocks are frequently found in calcareous areas as well as in areas where carbonate rocks are not exposed. However the recognition on the field of their genetic derivation when connections with the feeding source are no more evident, is often uncertain since the definition of the specific litofacies are not yet completely elucidated.
The detailed analysis of the lithofacies of calcareous tufa and travertines as well as the critical elaboration of existing geochemical data, shows that the petrologic features and stable isotopic signatures reflect the contrasting environmental conditions of deposition deriving from physico-chemical properties of the feeding waters that, although mostly of meteoric provenance, experienced different circulation/recharge history.
Travertines are well bedded, often finely laminated compact limestones, composed in the proximal part of the thermal system by peculiar crystalline crusts and in the distal part by bacterial/cyanobacterial laminites often associated with thin crystalline crusts, lenses of calcified-bubbles and paper-thin rafts.
In this system the carbonate deposition mainly derives from intense outgassing of the emerging supersaturated waters, and evaporation, concomitant with the rapid drop in temperature along the drainage network.
Travertine mineral content originates in deep geothermal/hydrothermal conditions where hot waters charged with HCO_3^- of meteoric and hypogean derivation, are able to dissolve high quantities of carbonate and/or evaporitic bedrock. The circulation of hot waters, allowed by open fractures/faults is ultimately controlled by extensional tectonics.
Calcareous tufa are poorly bedded, porous/chalky deposits containing frequent remains of macrophytes and invertebrates. They are made up of dominantly microcrystalline calcite of abiotic and biotic precipitation, forming phytohermal, stromatolitic or phytoclastic facies. It is commonly found in fluvial/palustrine depositional systems fed by carbonate-rich waters mostly deriving from karstic springs. The carbonate deposition deriving from mainly mechanical (vaporization/evaporation) and less significant biologic removal of CO_2 from flowing or standing waters, results to be controlled by the availability of meteoric water and ultimately by local and/or global climatic conditions.
The comparison of petrofacies and the critical elaboration of the related stable isotopic signatures of deposits still connected with the parent water and source systems, provide criteria for the univocal lithologic identification of their fossil counterparts so that the mainly climate-controlled Calcareous Tufa and the mainly tectonics-controlled Travertines can be easily detected even on the field.

Riassunto: A. Gandin & E. Capezzuoli, Travertini e Calcareous tufa: caratteristiche petrologiche e isotopiche*. (IT ISSN 0394-3356, 2007).*
Tra i carbonati continentali sono compresi i sedimenti prevalentemente formati da croste calcaree derivati da acque dolci scorrenti ricche in carbonato di calcio. In base alle caratteristiche fisiche di queste acque, è possibile distinguere i depositi originati da acque "calde" di provenienza idrotermale (travertini) da quelli precipitati da acque "fredde" di derivazione carsica (calcareous tufa). Questi due gruppi di calcari concrezionari sono caratteristici di sistemi deposizionali e geomorfologici molto differenti: sorgenti termali i primi, ambienti fluvio-palustri i secondi.
Affioramenti fossili di questi depositi si trovano comunemente, ma il riconoscimento sul terreno della loro derivazione genetica è spesso incerta a causa dell'assenza di una precisa definizione specifica delle relative litofacies.
L'analisi dettagliata delle litofacies dei travertini e dei calcareous tufa e la contemporanea elaborazione critica dei dati geochimici ricavati dalla letteratura mostra che le loro caratteristiche petrologiche e isotopiche riflettono le caratteristiche fisico-chimiche delle acque di origine le quali, anche se hanno la stessa derivazione meteorica, testimoniano di una differente ricarica e circolazione idrogeologica.
I travertini sono carbonati compatti, ben stratificati e in genere fittamente laminati. Essi si originano esclusivamente nelle vicinanze di sistemi idrotermali. Nella zone prossimali la fuoriuscita e lo scorrimento di acque calde sovrassature in carbonato di calcio determina la formazione di peculiari croste cristalline, mentre nelle porzioni più distali divengono predominanti le lamine batteriali/cianobatteriali spesso associate con sottili lamine cristalline, lenti di bolle gassose incrostate e impronte di vegetali. Gli alti tassi di accrescimento dei travertini sono condizionati dal veloce degassamento delle acque supersature e dall'evaporazione.
Il contenuto minerale delle acque riflette la natura delle condizioni idrotermali/geotermali nelle quali acquisiscono calore durante il loro percorso profondo. La temperatura di queste acque, ricche di HCO_3^- di derivazione meteorica o anche magmatica, infatti, permette la dissoluzione di grandi quantità di carbonati o solfati contenuti nelle rocce del substrato. La loro circolazione, intimamente connessa alla presenza di faglie/fratture beanti, è strettamente controllata dalla tettonica principalmente di tipo estensionale.
I calcareous tufa sono depositi generalmente porosi e scarsamente stratificati, contenenti abbondanti tracce di macrofite e invertebrati. Essi sono composti principalmente da calcite microcristallina di precipitazione abiotica e biotica che forma facies fitoermali, stromatolitica o fitoclastica caratteristiche di ambienti deposizionali fluvio-palustri con acque carbonatate derivanti da sistemi carsici. La deposizione, in genere lenta e con bassi tassi di accrescimento, è principalmente controllata dalla rimozione meccanica (vaporizzazione/evaporazione) e biologica (fotosintetica) della CO_2 da acque scorrenti o stagnanti. Tale processo risulta ovviamente condizionato dalla disponibilità di acqua meteorica e, di conseguenza, dalle condizioni climatiche.
Il confronto delle diverse petrofacies e l'elaborazione critica dei relativi contenuti isotopici derivati da depositi ancora connessi con le loro acque madri, fornisce un criterio per un'univoca identificazione litologica dei depositi fossili. In tal modo i calcareous tufa ed i travertini possono essere facilmente riconosciuti anche sul terreno, allo scopo di discernere quelle strette relazioni con il clima (calcareous tufa) e con la tettonica (travertini) che li caratterizza e che li ha posti al centro della ricerca internazionale nell'ultimo decennio.

Key words: Travertine, calcareous tufa, sedimentology, petrology, stable isotopes.

Parole chiave: Travertini, Calcareous tufa, Sedimentologia, Petrografia, Isotopi stabili.

1. INTRODUCTION

Continental carbonates are vulnerable rocks that in the geologic record rarely survive erosion and dissolution but are extensively recorded in the Quaternary continental successions of areas where the exposed and/or buried carbonate bedrock acts as calcium reservoir for the circulating groundwaters. However terrestrial limestones are presently forming on the Earth surface, in different geomorphologic/geodynamic settings under a wide range of conditions and are controlled by contrasting physico-chemical properties of the waters. Remnants of their fossil counterparts are frequently found in calcareous areas as well as in areas where carbonate rocks are not exposed, and disconnected from their primary setting. Consequently their origin and paleoenvironmental meaning can be difficult to assess since most of the published data do not account for the lithologic and petrographic features of the different types of terrestrial carbonates.

Continental limestones deposited as primary calcite crusts by flowing carbonate-rich waters are also known as flowstones. Lacustrine alike marine pelagic carbonates, settles in standing body of water below the high-energy zone (wave base). They are mostly represented by lime-mudstone composed of microcrystalline calcite (micrite).

Flowstones include speleothems, deposited in the subsurface environment of the karst system, and spring related carbonates deposited in open-air conditions but in different geomorphologic settings and contrasting physico-chemical properties of the waters. Groundwaters mostly of meteoric origin acquire, during more or less deep geothermal circulation pathway, different temperatures and saline concentrations rising at the spring as supersaturared/saturated carbonate waters, warmer (thermal) or cooler (karstic) than the ambient temperature.

In the current nomenclature the appellation of thermogene and meteogene travertines proposed by PENTECOST & VILES (1994) that however does not take in account the genetic sedimentary and environmental processes, is sometimes still used (MINISSALE *et al*., 2002; PENTECOST, 1995; 2005 and reference herein). The more realistic terminology of travertines, calcareous tufa and speleothems, proposed by RIDING (1991) and FORD & PEDLEY (1996), is based on the litho-genetic features of terrestrial flowstone carbonates and takes also in account the historical term of travertine.

Travertine is the long time appellation of a compact laminated calcareous lithology quarried since Etruscan times in Etruria (present-day Tuscany and northern Latium; GANDIN *et al*., 2006) and in Roman times near the town of Tibur (present name is Tivoli) where it is formed ("*lapis tiburtinus*") by hot waters rising from tectonically controlled presently active hydrothermal springs (FACCENNA *et al*., 1994), still called *Acquae albulae* (Latin for "whitish waters"). Thus the Tivoli area must be considered the geological type-locality of the thermal-related terrestrial limestone, the Travertine.

Calcareous tufa is the recent denomination of highly porous massive limestone deposited from cool or ambient temperature waters of karstic and/or meteoric derivation, in climate controlled alluvial/palustrine systems (PEDLEY, 1990; FORD & PEDLEY, 1996).

Speleothems, mainly stalactites, stalagmites and flowstones, are finely laminated macrocrystalline hypogean deposits built by successive rows of acicular/radiaxial, often ferroan calcite (FRISIA, 2003). It slowly precipitates from water drops in the dark subsurface, vadose conditions of the cave systems.

In many of the thermal or cool water spring-related subaerial sites where active deposition occur, older, often terraced deposits, even if affected by post-depositional processes (diagenetic cementation and/or karstic epigenetic dissolution and erosion), attest to the continuity of the sedimentation and show evidence of the different depositional pattern of the respective carbonate bodies. However since the meaning of the specific petrologic features of these sediments are not well known, they are often mixed up under the all-comprising term of travertine (JULIÀ, 1983; TURI, 1986; CILLA *et al*. 1994; CHAFETZ & LAWRENCE, 1994; PENTECOST, 2005; DUBAR, 2006 and references therein), disregarding detailed lithologic descriptions already published (FORD & PEDLEY, 1996; GUO & RIDING, 1998; 1999) and the potential information that their dissimilar depositional settings imply (CAPEZZUOLI & GANDIN, 2004).

The purpose of this article is to investigate on the relationships between the specific petrologic features and fabrics of "living" travertines and calcareous tufa and their distinctive physico-chemical properties and isotopic signature. The results of the critical elaboration of new and existing data will provide petrologic criteria supported by isotopic data, for the genetic, climatic or tectonic/geologic identification of “old” terrestrial carbonate deposits no more connected with their primary source systems.

2. DEPOSITIONAL AND ISOTOPIC CHARACTERISTICS OF TRAVERTINES AND CALCAREOUS TUFA

Subaerial flowstones originate in depositional systems characterized by contrasting environmental and physico-chemical properties and different sources of the mineral content of the waters. The specific petrologic features of spring-related calcareous deposits and the rate of crystal growth, results from the physico-chemical characteristics of precipitation processes that ultimately are controlled by the conditions of the flowing fluids, such as velocity of the flux, outgassing, ionic concentration and temperature. Temperature of spring and stream waters in turn, is controlled by the temperature the groundwater reaches in the hypogean circulation.

Source of the Ca-bicarbonate-rich waters are shallow (karstic) or deep (geothermal) subsurface circulation networks where waters charged of dissolved CO_2 of soil and/or meteoric derivation interact with the carbonate/evaporitic and/or magmatic bedrock and outflow from hydrothermal or karstic springs, as warm/hot or cool waters. The HCO_3^- and Ca^{+2} ions dissolved in more or less concentrated solutions are of mixed provenance mostly meteoric, partially recycled (dissolution of bedrock carbonates and/or evaporites) locally magmatic.

The hydrothermal system develops in areas where deep tensional fractures (HANCOCK *et al*., 1999; SHIPTON *et al*., 2004; ALTUNEL, 2005; BROGI & CAPEZZUOLI, 2008) or volcanic intrusions promote the hypogean circulation and heating of waters of meteoric and/or juvenile derivation. The mineral content of the outflowing thermal waters (min 20°C up to 90°C, PENTECOST, 2005) originates from the dissolution of high quantities of carbonate and/or evaporitic bedrock that often is not exposed on the surface. The subaerial circulation of the warm, sulphur/sulphate-rich thermal waters appears to be adverse to the vegetation, giving rise to an arid/desert white landscape (CAPEZZUOLI & GANDIN, 2005) (Fig. 1a).

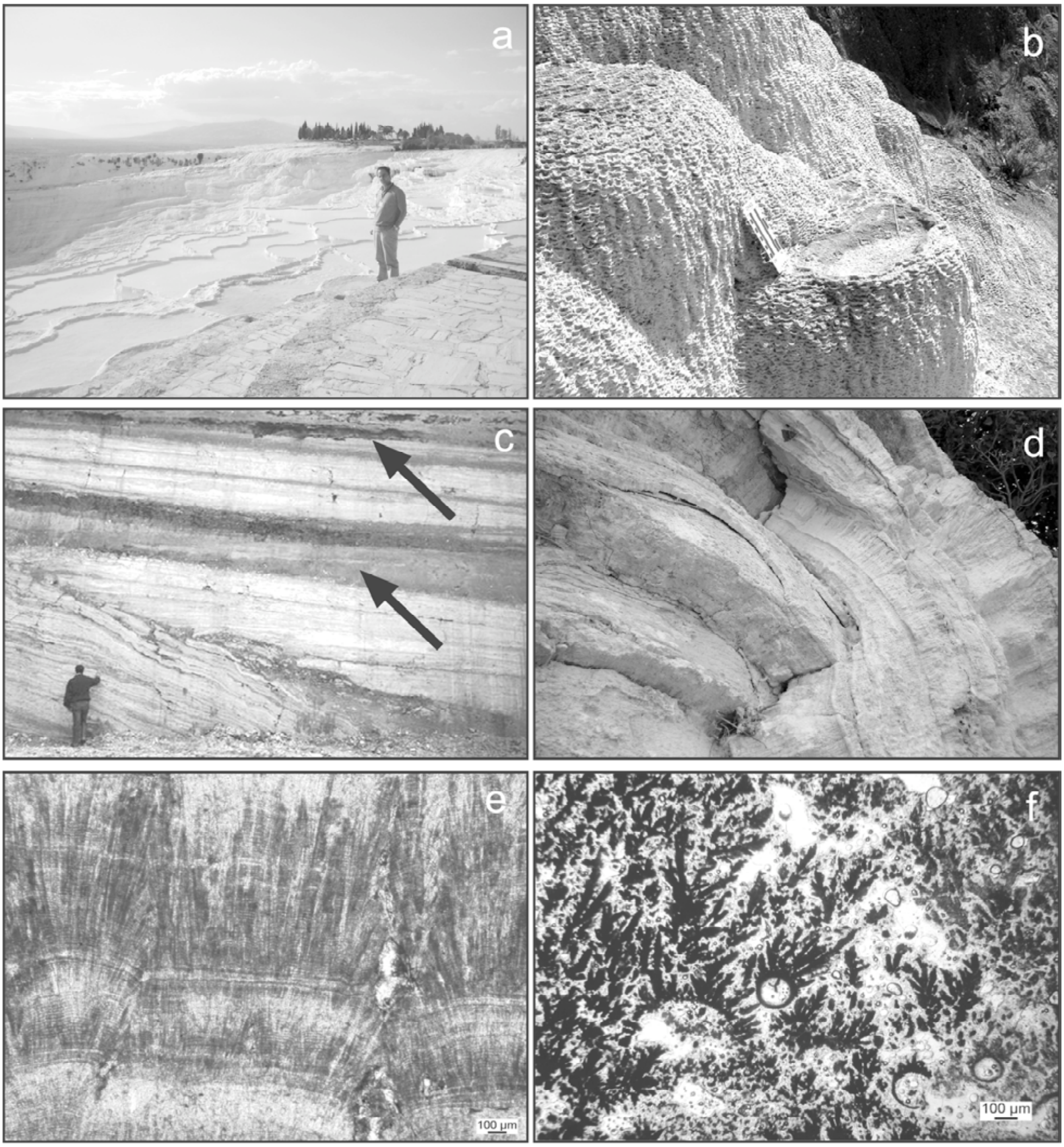

Fig. 1 -Examples of the thermal, "white desert" environment and related travertine deposits: a) shallow pools barred by crystalline rimstones along a low-gradient slope (Pamukkale, Turkey); b) the steep slope of a dried waterfall covered by micro terraces and larger/deeper bowl-like basins (Terme San Giovanni, Rapolano Terme, Italy); c) well bedded, laminated body of travertine showing a low-angle unconformity and dark intervals (black arrows) corresponding to lacustrine/pedogenetic episodes (Serre di Rapolano, Italy); d) transversal flexure-like section of a dam rimstone composed of regularly laminated crusts of crystal fans (Bagno Vignoni, Italy). Microfabrics of crystalline crust travertine: e) crystal fans made of finely laminated cloudy fibrous calcite (Rapolano Terme, Italy); f) feather-like bacterial/crystal shrubs partially growing on encrusted gas bubbles (Rapolano Terme, Italy).

Esempio di ambiente termale desertico "il deserto bianco ", e dei relativi depositi travertinosi; a) Pendio poco acclive con vasche disposte a terrazzo delimitate da bordi cristallini (Pamukkale, Turchia); b) Porzione acclive di una cascata inattiva coperta da micro- e macroterrazzi a forma di scodella (Terme San Giovanni, Rapolano, Italia); c) Corpi di travertino laminato e ben stratificato. Sono evidenti una discordanza a basso angolo e intervalli scuri (frecce nere) corrispondenti a episodi lacustri e/o pedogenetici (Serre di Rapolano, Italia); d) Sezione trasversale del bordo di una vasca formato da croste incurvate di calcite cristallina a ventaglio ben stratificata (Bagno Vignoni, Italia). Microfabric delle croste cristalline di travertino: e) Ventagli di calcite aciculare finemente laminata con concentrazioni di impurezze (Rapolano Terme, Italia); f) cespugli batteriali/cristallini a forma di piuma in parte accresciuti su bolle di gas incrostate (Rapolano Terme, Italia).

The karstic system, a shallow subsurface vadose network, developed in areas where carbonate rocks are exposed and the supply of meteoric water is rather abundant, yields mineralised waters which outflow at the spring with temperatures commonly cooler than the surrounding ambient but more or less stable throughout the year within the cave system (HORVATINCIC *et al*., 2003).

The Ca-rich waters giving rise to carbonate deposits, at the same time promote the establishment of a well developed riverine/palustrine depositional system and the growth of luxuriant vegetation (Fig. 2a, b).

Notwithstanding the extremely different physico-

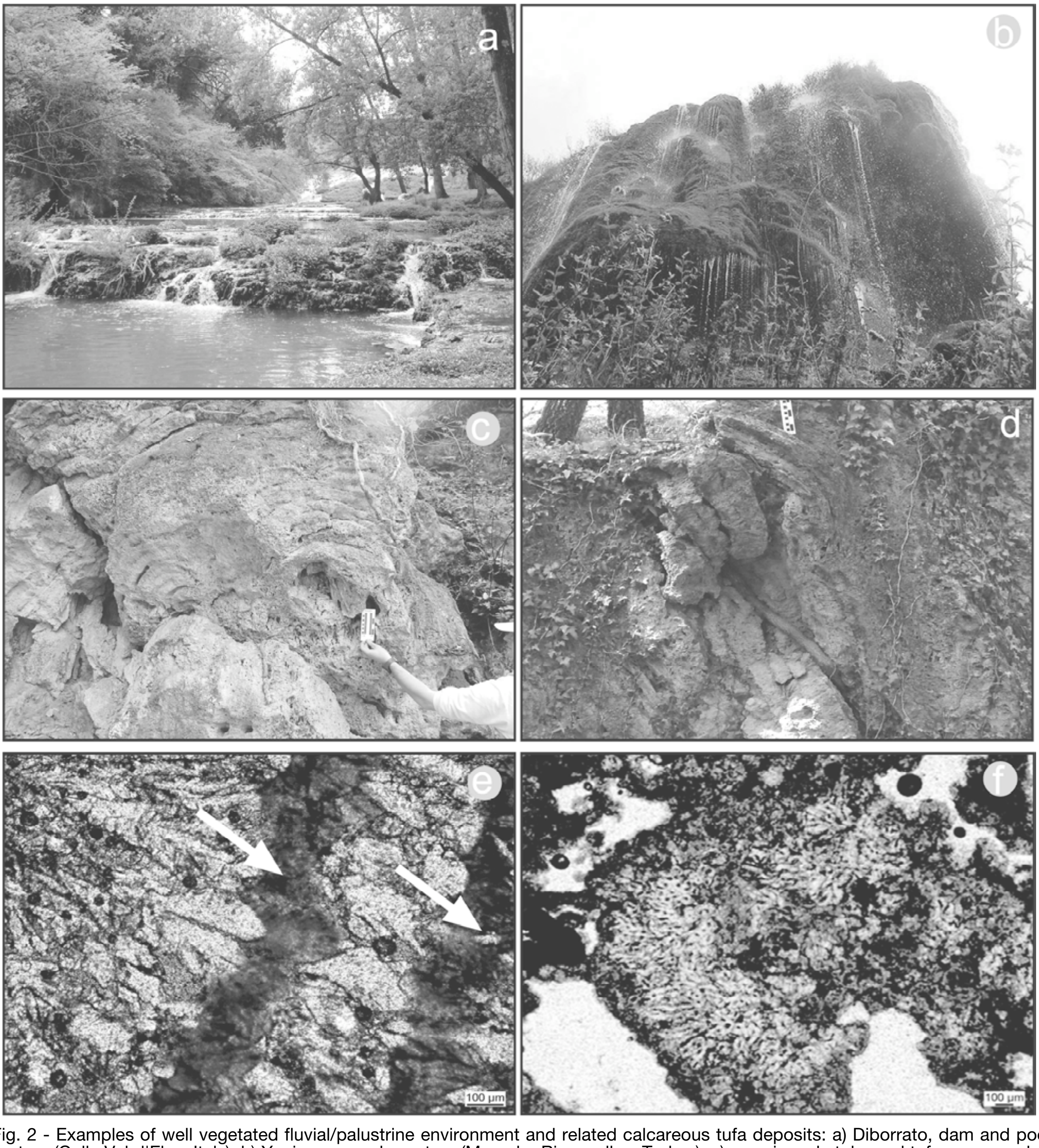

Fig. 2 - Examples of well vegetated fluvial/palustrine environment and related calcareous tufa deposits: a) Diborrato, dam and pool system (Colle Val d'Elsa, Italy); b) Yenice, cascade system (Meander River valley, Turkey); c) massive, phytohermal tufa composed of staked cushion-like elements (Diborrato, Colle Val d'Elsa, Italy); d) transversal flexure-like section of a dam rimstone composed of irregularly superposed biostromal layers (Diborrato, Colle Val d'Elsa, Italy). Microfabrics of calcareous tufa: e) organic remains (white arrows) alternated with rows of limpid crystalline calcite ("stromatolitic" facies; Colle Val d'Elsa, Italy); f) *Rivularia* filaments enclosed in limpid sparite (Phytohermal facies, La Pigna falls, Monticiano, Italy).

Esempi di ambienti fluviali/palustri ben vegetati e dei relativi depositi di calcareous tufa: a) Sistema di vasche e bordi rialzati (rimstones) presso il Diborrato (Colle Val d'Elsa, Italia); b) Sistema di cascata presso Yenice (Fiume Meandro, Turchia); c) calcareous tufa fitoermali mal stratificati composti da elementi a cuscino sovrapposti (Diborrato, Colle Val d'Elsa, Italia); d) Sezione trasversale del bordo di una vasca formato da croste biostromali incurvate e irregolarmente sovrapposte (Diborrato, Colle Val d'Elsa, Italia). Microfabric di calcareous tufa: e) alternanza di livelli scuri con residui organici (frecce bianche) e di livelli di calcite cristallina limpida (facies "stromatolitica", Colle Val d'Elsa, Italia); f) Filamenti di Rivularia *inclusi in cristalli di calcite spatica (Facies Fitoermale, Cascata de La Pigna, Monticiano, Italia).*

chemical properties of the waters of the two spring systems, some of the physical processes connected with the precipitation of calcium carbonate give rise to similar depositional structures in the carbonate bodies that however are characterized by completely different fabrics and biologic involvement (Fig. 1, 2).

Precipitation of calcium carbonate mainly derives from the removal of CO_2 from carbonate-rich waters and its amount is consistent with the concentration and temperature of the parent water.

Abiotic/physical precipitation is dominant under turbulent flow regime whereas evaporation and effective biomediation/photosynthetic action requires sluggish flow or static water (PEDLEY, 1990).

Vaporization and outgassing, largely dominant processes connected with falls, rapids and the presence of obstructions on the stream paths, contribute to the passive encrustation of every object vegetal, animal or rock the flow runs into. The rapid removal of CO_2 acting during the water drift or within static waters of intervening basins, moreover, induces the precipitation of solid encrusting calcite in a succession of arcuate rims/barrages/terraces (rimstones) that delimit pools/ponds of variable sizes and depths (Fig. 1a,b; Fig. 2a,b), depending on the amount of flowing water and the gradient of the drainage path (HAMMER *et al*, 2007; PEDLEY *et al*., 1996; PENTECOST, 2005).

Evaporation is also a physical process induced by higher temperatures of the water at the air/water interface of shallow small or large basins. Consequent, occasional whitenings result in abiotic microcrystalline calcite that, together with possible biotic micrite produced by the photosynthetic activity of aquatic organisms, settle as lime mud on the bacterial biofilms supports made of extracellular polymeric substances (EPS) at the bottom of the basin.

Growing evidence indicates that active biologic/photosynthetic contribution to the carbonate precipitation results to be effective even if actually negligible, mostly in the fluvial/palustrine system where dominant macrophytes prosper because of the cool and humid conditions of the environment (MERZ- PREISS & RIDING, 1999). In the hot waters of thermal springs and in their arid surroundings, conditions of life are extreme and the organisms involved, mostly heat-loving bacteria, play a passive role of support to the precipitating calcite.

Bacterial colonies are commonly found in both systems; they settle in lower-energy microhabitats/niches sheltered from the tractive flow on the bottom of the basins, or on the sides of channels, and passively incorporate carbonate particles in the mucilaginous biofilm (EPS) they produce (MERZ-PREISS & RIDING, 1999).

The sediment that settles within the floodbasins is in part carbonate sand transported by the flow but most of it has specific features that reflect the original concentration of the water and the difference between water and ambient temperatures.

In the assumption that the $\delta^{13}C$ and $\delta^{18}O$ values of subaerial flowstones must reflect the different physicochemical properties of the parent waters, a survey has been carried out of the published stable isotope data on recent deposits of well known origin collected in the most significant present day sites of formation (Fig. 3, 4) with the intent to find the possible relationships between the overall depositional conditions of each spring system and the resulting sedimentary and petrologic features.

The geochemical ratio of the stable isotope pairs of carbon and oxygen (^{12}C, ^{13}C and ^{16}O, ^{18}O) depends mostly on the physico-chemical conditions of water (temperature and saline/CO2 concentration) that promote isotopic fractionation. Ratios compared to a standard sample (PDB = a Cretaceous belemnite; SMOW = Standard Mean Ocean Water, only for oxygen) are expressed in the δ PDB or SMOW (‰) notation providing an expanded scale for the comparatively small differences observed. Fractionation, resulting from the loss for evaporation, degassing or metabolic consumption of the lighter isotopes during the (bio)geochemical cycle, induces discrete changes of C and O ratios. Their values therefore provide information about the physico-chemical conditions of the precipitation events (rate and temperature) and the influence of potential metabolic processes, hence about the sources of water and carbon dioxide as well. It also provides information on the temperature at which deposition occurred and assists in radiometric dating (more references in: FOUKE *et al*., 2000; ANDREWS, 2005; PENTECOST, 2005).

3. TRAVERTINE

Present day hydrothermal systems where travertine is forming (the San Giovanni Terme spring system at Rapolano near Siena - Fig. 1b,c,d - is an excellent example; BARAZZUOLI *et al*., 1988), are fed by warm to hot carbonate-rich waters, often charged with other ionic compounds such as sulphate/sulphide, chlorine, etc., surfacing from linear or punctiform vents.

The mineral content of the hot waters originates in deep geothermal/hydrothermal conditions where heated waters charged with HCO_3^- of meteoric and hypogean/magmatic derivation, are able to dissolve high quantities of carbonate and/or evaporitic bedrock. Their circulation, allowed by open fractures/faults, is ultimately controlled by extensional tectonics (SIBSON, 2000; HANCOCK *et al*., 1999; BROGI *et al*., 2005; BROGI & CAPEZZUOLI, 2008).

In this system carbonate deposition, marked by a high-rate production, mainly derives from intense outgassing of CO_2 and evaporation of the emerging waters which concurs to the rapid drop in temperature of the supersaturated waters flowing along the drainage network.

The biological contribution in the thermal spring environment is not relevant since the subaerial circulation of warm/hot, unhealthy carbonate-saline waters prevents the development of macrophytes. Only heat-loving bacteria develop on humid surfaces or warm water puddles and pools (CHAFETZ & FOLK, 1984). Moreover, precipitation of calcite is so rapid that even bacteria and cyanobacteria have no time/possibility to colonize the carbonate surface that remains a bare white desert landscape (Fig. 1).

In the desert thermal landscape the rapid removal of CO_2 results from the simultaneous processes of outgassing, vaporizing/cooling combined with the surface flow characteristics that in turn are controlled by the morphologic gradient of pre-existing or self-built slopes

(Fig. 1a,b). Velocity and turbulence of the flow control the shape and distribution of the sedimentary bodies. Smooth flows running on flat to inclined surfaces, where obstructions are rare and commonly of small size (Fig. 1a), gives rise to plane, regularly laminated beds, locally showing a large scale lenticular trend (Fig. 1c). The resulting carbonate edifices vary in shape from suspended channels to cones and ridges made up of coalescing smaller cones or vents. Conversely turbulent flows give rise to waterfalls and rimstones (Fig. 1b) of any size (large rimmed terraces to microterraces) made of calcite beds arranged in a succession of structural flexures (Fig. 1d) producing arcuate barrages that delimit shallow floodbasins (Fig. 1a,b).

The sedimentary architecture resulting from this depositional system defines the carbonate lithotype designated as travertine. It is characterized by well bedded, finely laminated limestones, composed in the proximal part of the thermal system by peculiar macrocrystalline crusts and in the distal part by bacterial/cyanobacterial microcrystalline/mud-supported sediment (GUO & RIDING, 1998; 1999; ÖZKUL *et al*., 2002). The specific petrologic features are represented by regularly laminated, commonly flat bodies built up by a compact, laminated crystalline fabric composed of feather-like crystals (Fig. 1f) or crystal bushes grown from smooth flows along low gradient drainage channels or of crystal fans (Fig. 1e) deriving from turbulent flood in waterfalls. Interbedded lenticular bodies of microcrystalline, granular or mud supported deposits correspond to the backfill of ponds and puddles that varies in texture and content depending on their distance from the vent, hence on the temperature and concentration of the water. On the standing waters of proximal basins, whitenings related to evaporation hence rapid removal of CO2, induce the precipitation of microcrystalline calcite on bacterial biofilm supports (EPS) at the bottom of the basin, giving rise to a characteristic spongy fabric (see fig. 4c in GANDIN *et al.*, 2006).

Brittle crystalline crusts often form on the hot water surface floating pack-like until, under the increasing load of calcite and cyanobacterial growth, sink at the bottom in stacks of slabs, giving rise to the paper-thin raft fabric described by GUO & RIDING (1998). In secluded parts of channels the combined actions of bacterial/biological activity outgassing and evaporation induce the formation of peculiar foam-like structures made of gas bubbles coated by a microcrystalline calcite film and sometimes encrusted also by feather-like crystals (Fig. 1f).

In the more distal basins the lime mud-fill contains remains of ostracods, gastropods, *Chara* and diatoms attesting the presence of life and consequently of cooler less mineralised waters. Associated with the lacustrine-like facies, more or less developed pedogenetic/root concretions, document episodic desiccation and pedogenetic processes deriving from the interruption and/or diversion of the water flux.

Geochemical analyses of presently forming travertines have been performed on samples collected from several thermal localities as the Yellowstone Park hydrothermal springs systems (FRIEDMAN, 1970; FOUKE et al., 2000); in Italy Le Zitelle springs near Viterbo and Bagni San Filippo on the Monte Amiata (Siena), related to volcanic complexes (GONFIANTINI *et al*., 1968; CHAFETZ & LAWRENCE, 1994) and the Rapolano/Acqua Borra (Siena) geothermal springs (GUO et al., 1996); in Spain near Granada (JIMENEZ DE CISNEROS *et al*., 2006). The temperature of the parent groundwaters at the emergence of the studied thermal springs (Fig. 3) vary from 34°C (Spain) up to 60°C (Le Zitelle) and 73°C (Yellowstone).

Stable isotopic data obtained from calcite precipitated from hot/warm waters in these localities, have been plotted on a Cartesian coordinate system where it is possible to observe that the $\delta^{13}C$ versus $\delta^{18}O$ PDB values falls in the same field of distribution characterized by dominantly positive $\delta^{13}C$ values (Fig. 3).

The $\delta^{18}O$ (PDB) range from -4‰ to -30‰, appears to be influenced by high temperatures and supersaturation levels of the outflowing waters (FRIEDMAN, 1970; GUO *et al*., 1996; FOUKE *et al*., 2000). The increase of $\delta^{18}O$ values indicates evaporation of the lighter isotope ^{16}O and cooling of the waters, whereas heavier values of $\delta^{13}C$ reflect removal of the lighter isotope ^{12}C, and consequent outgassing of CO_2 (GONFIANTINI *et al.*, 1968; USDOWSKI *et al.*, 1979; TURI ,1986; CHAFETZ & LAWRENCE, 1994).

The typical range from -2‰ to +8‰, of $\delta^{13}C$ values in travertines, is interpreted to reflect the contamination of the isotopic composition of groundwater by the bedrock marine limestones or juvenile/magmatic waters (GONFIANTINI *et al.*, 1968; FRIEDMAN, 1970; TURI, 1986; GUO *et al*., 1996). It is worth noting that soil derived carbon has never been reported from thermal groundwater composition (PENTECOST, 2005).

The contribute of recycled isotopes is also supported by the proximity of the distribution field of the isotopic values of travertines and recent marine carbonate sediments and older limestones (Fig: 5), which records similar evaporative conditions of calcium carbonate precipitation in warm marine waters and also the recycling through dissolution, of the heavier fossil ^{13}C isotope. This specific distribution of stable isotopic values of travertine, while attesting the thermal imprint of the carbonate parent fluids, register dominantly physico-chemical precipitation of carbonates and a relevant contribution of ions deriving from carbonate bedrock and/or juvenile/magmatic waters.

4. CALCAREOUS TUFA

Present day riverine/palustrine systems where calcareous tufa are actively forming (the Diborrato water system - Fig. 2a, c, d - in Colle Val d'Elsa area, near Siena is an instructive example), are fed by carbonate-rich waters of meteoric derivation mostly rising from karstic springs, or in some cases resulting at least in part, from diluted and cooled, originally thermal waters (CAPEZZUOLI *et al*., 2008). The mean temperature of groundwaters at the emergence of karstic springs is on average, cooler (2°C lower in the Dinaric Karst; HORVATINCIC *et al*., 2003) than the flowing waters from which tufa precipitates. However it rapidly equilibrates with the local atmospheric temperature that is influenced by seasonal changes and controlled by the latitudinal position and global climatic regime. The subaerial circulation of cool/ambient temperature waters, promote the development of vegetation and subsequent precipita-

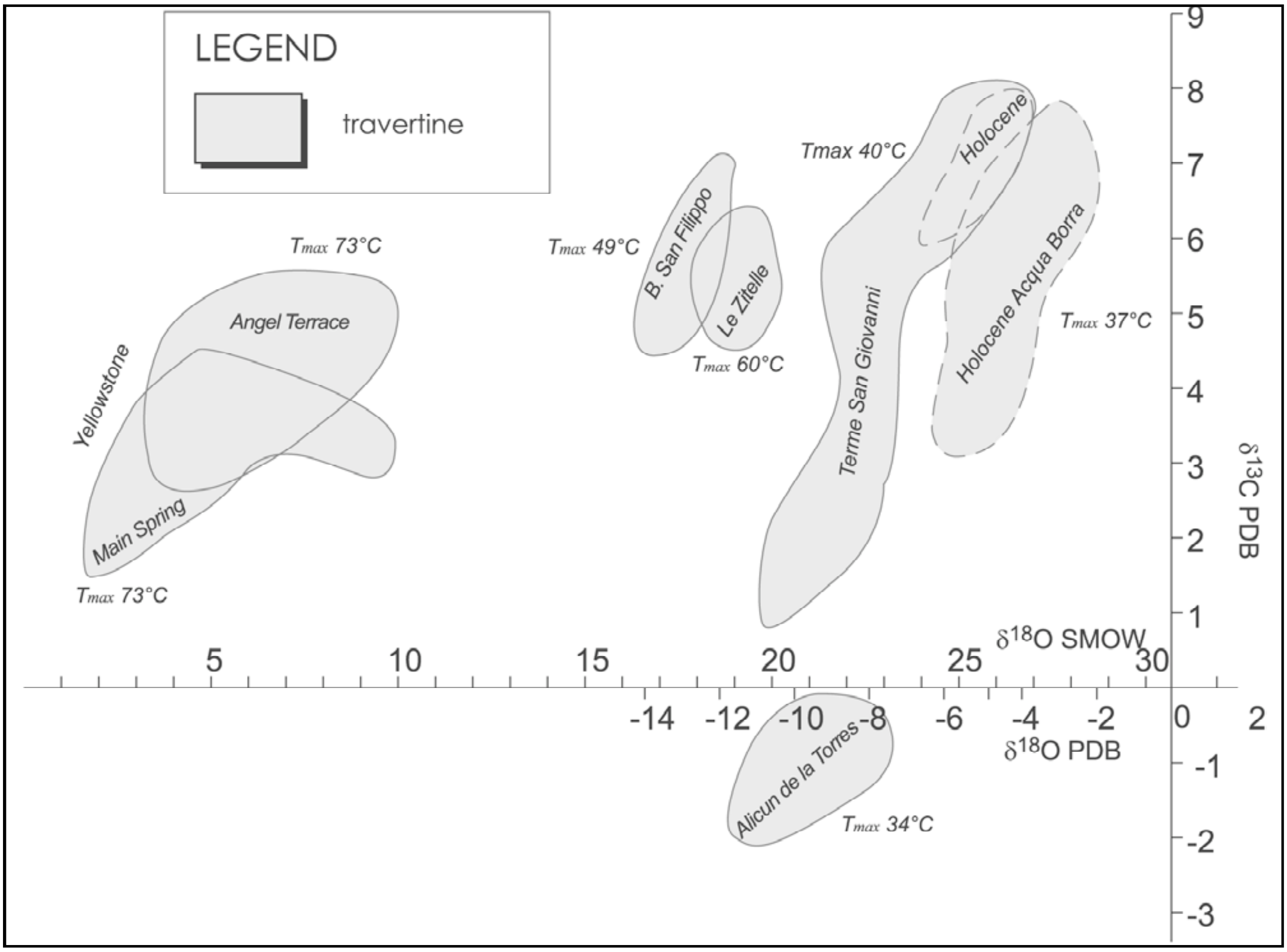

Fig. 3 - Combined plot of $\delta^{18}O$ (SMOW/PDB) and $\delta^{13}C$ (PDB) values derived from travertine sampled in selected active thermal localities of the world. Data sources: Yellowstone (Angel Terrace - Fouke *et al.*, 2000; Main spring - Friedman, 1970); Bagni San Filippo (Siena, Italy) (Gonfiantini *et al*., 1968); Le Zitelle (Viterbo, Italy) (Chafetz & Lawrence, 1994); Terme San Giovanni (Siena, Italy) (Guo *et al*., 1996); Acqua Borra (Siena, Italy)(unpublished data); Alicun de la Torres (Spain) (Jimenez de Cisneros *et al*., 2006).

Diagramma combinato dei valori di $\delta^{18}O$ (SMOW/PDB) e $\delta^{13}C$ (PDB) di travertini campionati in alcune località termali attive nel mondo. Dati ricavati da: Yellowstone (Angel Terrace - Fouke et al.*, 2000; Main spring - Friedman, 1970); Bagni San Filippo (Siena Italia) (Gonfiantini* et al.*, 1968); Le Zitelle (Viterbo, Italia) (Chafetz & Lawrence, 1994); Terme San Giovanni (Siena, Italia) (Guo* et al.*, 1996); Acqua Borra (Siena, Italia) (dati originali); Alicun de la Torres (Spain) (Jimenez de Cisneros* et al.*, 2006).*

tion of calcium carbonate that however show a low-rate production.

The removal of CO_2 from flowing or standing waters is controlled by the dominant action of physical processes as vaporization/evaporation combined with a minor contribution from the biologic/photosynthetic activity of the emerged vegetation. In places where the energy of the waters is higher, the tumultuous and more copious release of CO_2 stimulates the development of luxuriant vegetation. Emergent as well as aquatic plants and reeds, colonies of microbes, mosses and algae settle preferentially on raised irregularities of the stream bottom and on dam/barrages rims. Vaporization/outgassing processes enhanced by the irregularly scattered vegetal clusters and thickets acting as obstacles to the current flux (Fig. 2a,b), lead to the gradual, more or less pervasive calcification of massive pillow-like phytohermal/stromatolitic edifices (Fig. 2a, b, c).

Filaments, stems and rows of green organic matter progressively encrusted by microcrystalline or larger crystals of limpid prismatic calcite can be detected within "ancient" as well as in "living" (Fig. 2e,f) phytohermal deposits. In the backward floodbasins delimited by phytohermal barrages, rather quiet palustrine-/lacustrine-like conditions of sedimentation occur. *Chara* meadows and concentrations of diatoms sometimes develop on the bottom floored by lime mud with a characteristic peloidal fabric.

The typical porous/chalky fabric consists of microcrystalline, low-Mg calcite and peloidal aggregates of abiotic and biotic production. Abundant vegetal remains are preserved mainly as casts of fragments and parts of macrophytes or as filaments encased within limpid calcite spar (Fig. 2e, f). Remains of invertebrates are frequently found. Many of the vegetation components are organisms such as diatoms and characeans that favour cool fresh-waters and mosses/Bryophytes that cannot tolerate temperatures higher than 20°C (Glime & Vitt, 1984). Therefore the biologic contribution in the precipitation of carbonates in the riverine/palustrine system where macrophytes prosper, results to be mainly a passive role of support controlled by the availability of meteoric water.

The sedimentary architecture resulting from this depositional system defines the carbonate lithotype designated as calcareous tufa. It consists of highly porous, poorly bedded, irregularly staked lenticular bodies of massive phytohermal or stromatolitic buildups (Fig. 2c) associated with thin lenticular layers of unsorted phytoclastic sands and/or mud-supported pond-related sediments (Buccino *et al*., 1978; D'Argenio *et al*., 1983; Ferreri 1985; Brancaccio *et al*., 1986; D'Argenio & Ferreri, 1988; Violante *et al*., 1994; 1996).

The environmental requirements for the deposition of calcareous tufa are ultimately regulated by climatic local or global conditions (Horvatincic *et al*., 2003).

Geochemical analyses of presently forming calcareous tufa have been performed on samples collected from several riverine/stream systems in central-northern Europe. The parent water temperatures of the studied carbonate samples (Fig. 4), range from average 10°C in northern/central Europe up to 20°C in the Mediterranean area (9°C in Poland and UK, Thorpe *et al*., 1980; Pazdur *et al*., 1988; Andrews *et al*., 1994; Garnett *et al.*, 2004; 10°C in Germany and Belgium, Andrews *et al*., 1994; Janssen & Swennen, 1997; 15°C in Spain, Sancho *et al*., 1997; Andrews *et al.*, 2000; Arenas *et al*., 2000; Peña *et al*., 2000).

Stable isotopic data obtained from the calcite precipitated from cool spring/stream waters in these localities, have been plotted on a Cartesian coordinate system where it is possible to observe that the $\delta^{13}C$ versus $\delta^{18}O$ PDB values all falls in the same field of distribution characterized by negative $\delta^{13}C$ values (Fig. 4).

The typical range of $\delta^{13}C$ values in calcareous tufa, from -11‰ to -5‰, reflect the outgassing of already light ^{12}C of meteoric and soil derivation (Pentecost, 2005), since the preferential uptake of ^{12}C by green plants through photosynthetic action does not appear to affect the overall carbon distribution and removal in a freshwater system (Usdowski *et al.*, 1979; Chafetz & Lawrence, 1994; Andrews *et al*., 2000).

The $\delta^{18}O$ (PDB) values ranging from -3‰ to -12‰, register cool temperature and saturation levels of the spring waters (Gonfiantini *et al*., 1968; Usdowski *et al.*, 1979; Turi ,1986; Chafetz & Lawrence, 1994) and consequently record the properties of the local climatic regime (Horvatincic *et al*., 2003).

Stable isotopes value of the calcareous tufa essentially reflects the composition of the parent karstic water which ionic content mainly results from isotopically light, soil derived CO_2 contained in recharging meteoric waters. A minor input of heavier recycled ^{13}C derives from dissolution of the marine carbonate bedrock (Horvatincic *et al*., 2003), but has no influence in the isotopic distribution (Fig. 5). Consequently, the specific distribution of the stable isotopic values of calcareous tufa, while attesting the cool, fresh-water karstic and ultimately meteoric imprint of the carbonate parent fluids, corroborates also the dominantly passive biological contribution to the precipitation of calcium carbonate, and cool climatic conditions at the time of deposition.

5. CONCLUSION

Travertine and calcareous tufa are flowstones that form under open-air conditions at the emergence of thermal springs or along fluvial valleys/cool water springs systems: two distinct geomorphologic settings fed from groundwaters that after a non comparable recharge/circulation pathway, emerge with different mineral content and different temperatures. On the surface the flow of warm-to-hot or cool/ambient temperature waters produce contrasting biological responses: a bare white desert around thermal springs or luxuriant vegetation along the stream valley. The lithologic features and isotopic signature of travertine and calcareous tufa, closely record the specific physico-chemical composition and biologic imprint of the related depositional environments. Criteria for the univocal definition of calcareous tufa and travertines can be acquired through the comparison of the characteristics of the respective present day depositional settings, the lithologic/petrographic features and related isotopic signature of the carbonates in formation.

Travertines deposited in thermal spring systems, are characterized by warm-to-hot water supersaturated with calcium bicarbonate and free CO_2. Outgassing and vaporizing/cooling processes combined with turbulence and velocity of the flow control the shape and distribution of the sedimentary bodies. They consist of well bedded, finely laminated, dominantly crystalline crusts often associated with calcified-bubble facies, paper-thin rafts, and in the distal part, with peloidal aggregates and bacterial/cyanobacterial laminites. Travertine depositional features and the positive field of distribution of $\delta^{13}C$ register the dominant control of the physico-chemical parameters: temperature, evaporation and outgassing, on calcite precipitation. The hot, supersaturated carbonate waters rising from deep subsurface circulation through a network of extensional faults are in part of meteoric derivation and in part of recycled, juvenile geothermic/magmatic provenance.

Calcareous tufa develop in fluvio-palustrine systems fed by cool, carbonate-rich waters mainly of karstic and meteoric origin. In evident contrast with the thermal system where life is limited to mainly heat-loving bacteria, in the fluvio/palustrine conditions luxuriant vegetation of micro- and macrophytes results from the opportunistic colonization of water-rich environments where large amounts of CO_2 are available. The irregular distribution of the sedimentary bodies along the valleys and their petrologic features, reflect the physico-chemical properties of the water and hydrodynamics of the flow. Highly porous, poorly bedded, irregularly staked phytohermal or stromatolitic buildups and lenticular layers of unsorted phytoclastic sands and/or mud-supported pond-related sediments, characterize the tufa lithofacies. Microcrystalline calcite, peloidal aggregates and/or limpid spar are the dominant fabrics.

The negative field of distribution of stable isotopes values of calcareous tufas essentially reflects the parental relationships with the meteoric and soil-derived karstic waters and a minor input of heavier recycled carbon. The vegetation involvement in the formation of calcareous tufa appears to be limited to a passive role of support more than an active involvement in the chemical biogenic precipitation of calcium carbonate. Accordingly, the development of calcareous tufa appears to be controlled by the availability of meteoric water and ultimately by local/global climatic conditions.

Facies analysis and petrographic characterization

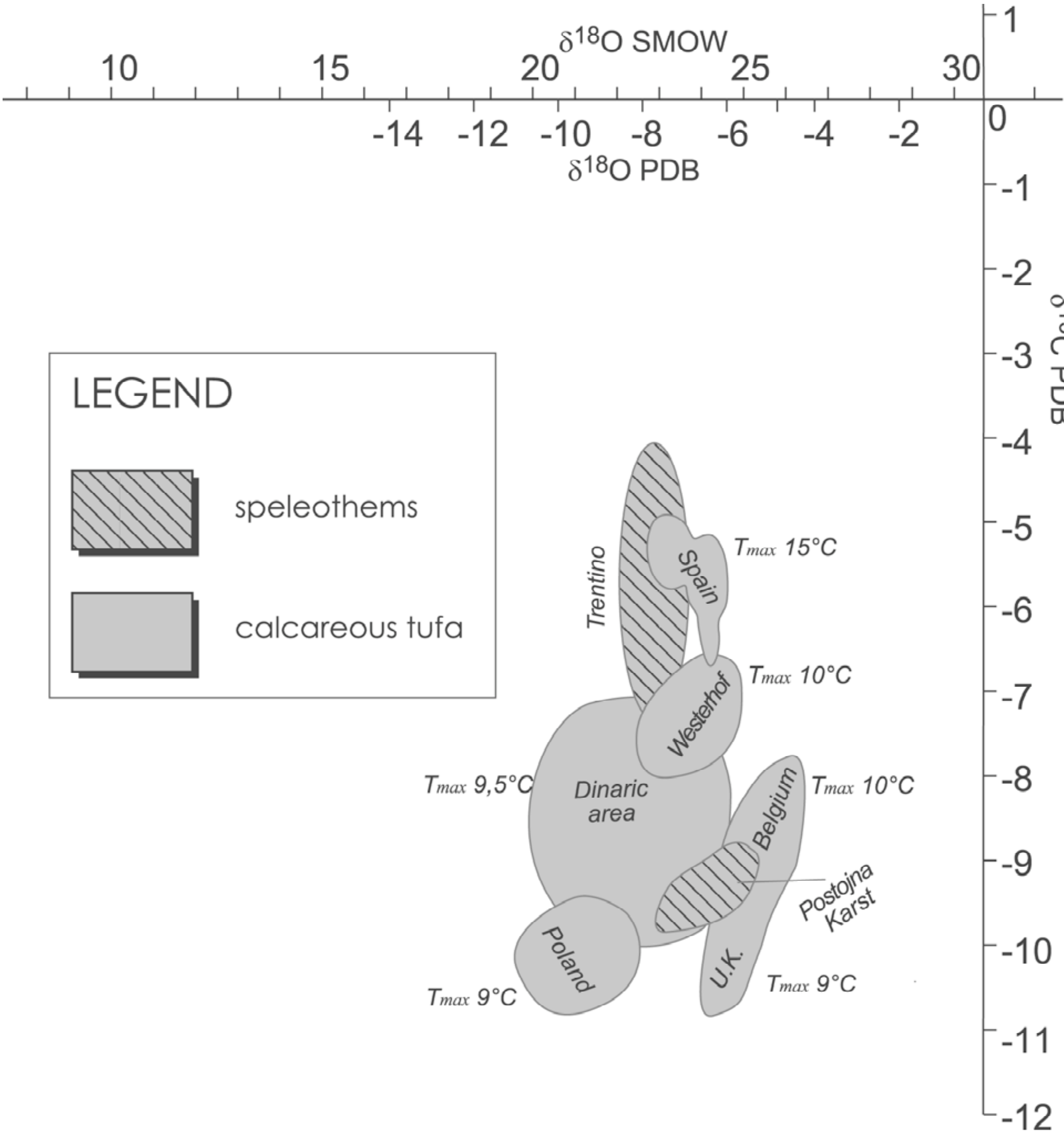

Fig. 4 - Combined plot of $\delta^{18}O$ (SMOW/PDB) and $\delta^{13}C$ (PDB) values derived from tufa and speleothems in formation, sampled in selected localities of central-north Europe. Data sources: Poland (Pazdur *et al*., 1988); Dinaric area (Horvatinčić *et al*., 2003); UK/Belgium (Andrews *et al*., 1994; Thorpe *et al*., 1980; Janssen & Swennen, 1997; Garnett *et al*., 2004); Spain (Peña *et al*., 2000; Sancho *et al*., 1997; Arenas *et al.*, 2000; Andrews *et al.*, 2000); Trentino (Italy) (Frisia, 2003); Postojna Karst (Horvatinčić *et al*., 2003); Westerhof (Germany) (Usdowski *et al*., 1979).

Diagramma combinato dei valori di $\delta^{18}O$ (SMOW/PDB) e $\delta^{13}C$ (PDB) ricavati da calcareous tufa e speleotemi in formazione, campionati in alcune località dell'Europa centro-settentrionale. Dati ricavati da: Polonia (Pazdur et al., *1988); Area Dinarica (Horvatinčić* et al., *2003); GB/Belgio (Andrews* et al., *1994; Thorpe* et al., *1980; Janssen & Swennen, 1997; Garnett* et al., *2004); Spagna (Peña* et al., *2000; Sancho* et al., *1997; Arenas* et al., *2000; Andrews* et al., *2000); Trentino (Italia) (Frisia, 2003); Grotte di Postumia (Horvatinčić* et al., *2003); Westerhof (Germania) (Usdowski* et al., *1979).*

of the present day terrestrial limestones forming from flowing waters in subaerial settings, evidence the unmistakable differences in fabrics, lithofacies and biologic involvement in the deposition of travertine and calcareous tufa. Likewise, the fields of distribution of the $\delta^{13}C$ and $\delta^{18}O$ isotopic values of recent deposits of well known origin appear to be rather well correlated with the distinctive environmental conditions and petrographic features of each group: they reflect unrelated physico-chemical conditions of the fluids feeding the two depositional systems.

The distribution field of the stable isotopes of tra-

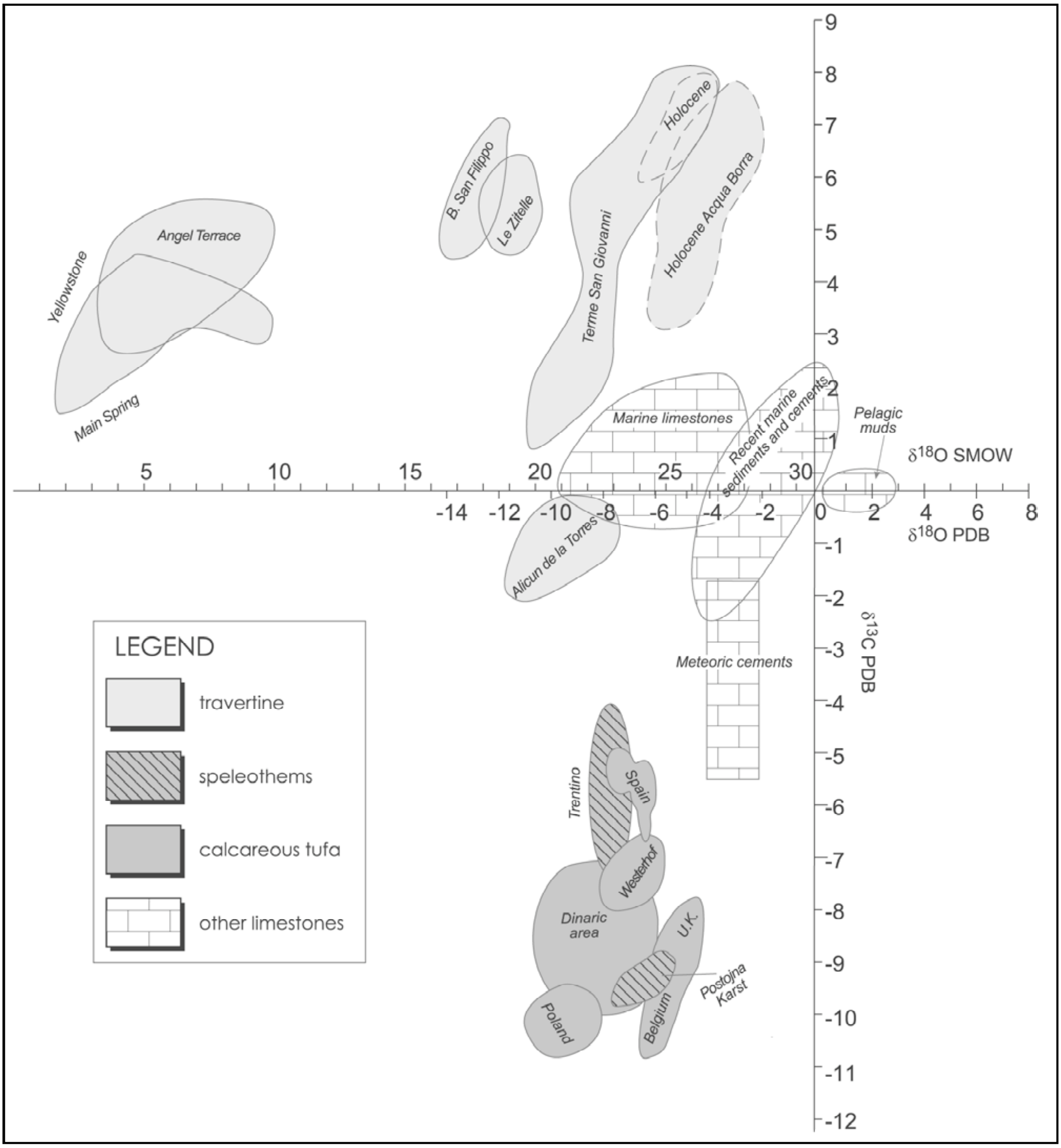

Fig. 5 - Combined plot of $\delta^{18}O$ (SMOW/PDB) and $\delta^{13}C$ (PDB) values derived from carbonates presently forming in terrestrial (travertine, calcareous tufa, speleothems) and marine (skeletal-ooid sediments and pelagic muds) environments and from lithified marine limestones. Data sources for travertine see Fig. 2. Data sources for tufa and speleothems see Fig. 4. Data sources for marine limestones, recent calcareous sediments and meteoric cements: Nelson & Smith (1996 with references therein).

Diagramma combinato dei valori $\delta^{18}O$ (SMOW/PDB) e $\delta^{13}C$ (PDB) dei carbonati attualmente in formazione in ambiente continentale (travertini, calcareous tufa, speleotemi), e marino (depositi scheletrici, ad ooidi e fanghi pelagici): Sono inclusi per confronto anche i valori dei calcari marini litificati e dei cementi di origine meteorica. Per dati sui travertini vedi Fig. 2. Per i dati sui calcareous tufa e gli speleotemi vedi Fig. 4. Per i carbonati marini, e i cementi meteorici vedi Nelson & Smith (1996) cum bibl.

vertine appears to be wider than that of calcareous tufa. It probably reflects the more ample range of temperature, dept of circulation, volcanic or groundwater sources of the travertine-related waters, while the karstic-meteoric waters of the calcareous tufa records more uniform climate-related conditions.

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