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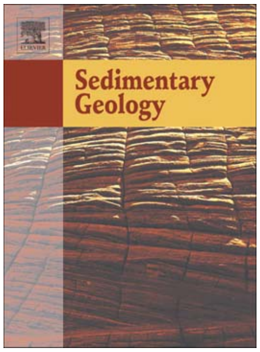

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What do we really know about early diagenesis of non-marine carbonates?

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Abstract

Non-marine carbonate rocks including cave, spring, stream, calcrete and lacustrine-palustrine sediments, are susceptible to early diagenetic processes. These can profoundly alter the carbonate fabric and affect paleoclimatic proxies. This review integrates recent insights into diagenesis of non-marine carbonates and in particular the variety of early diagenetic processes, and presents a conceptual framework to address them. With ability to study at smaller and smaller scales, down to nanometers, one can now observe diagenesis taking place the moment initial precipitates have formed and continuing thereafter. Diagenesis may affect whole rocks, but it typically starts in nano- and micro-environments. The potential for diagenetic alteration depends on the reactivity of the initial precipitate, commonly being metastable phases like vaterite, Ca-oxalates, hydrous Mg-carbonates and aragonite with regard to the ambient fluid. Furthermore, organic compounds commonly play a crucial role in hosting these early transformations. Processes like neomorphism (inversion and recrystallization), cementation and replacement generally result in an overall coarsening of the fabric and homogenization of the wide range of complex, primary microtextures. If early diagenetic modifications are completed in a short time span compared to the (annual to millennial) time scale of interest, then recorded paleoenvironmental signals and trends could still acceptably reflect original, depositional conditions. However, even compact non-marine carbonate deposits may behave locally and temporarily as open systems to crystal-fluid exchange and overprinting of one or more geochemical proxies is not unexpected. Looking to the future, relatively

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few studies have examined the behaviour of promising geochemical records, such as clumped isotope thermometry and (non-conventional) stable isotopes, in well-constrained diagenetic settings. Ongoing and future in-vitro and in-situ experimental approaches will help to investigate and quantify sequences of intermediate diagenetic products, processes and controls, and to quantify rates of early diagenesis, bridging a gap between nanoscale, molecular lab studies and the fossil field rock record.

Key words: continental carbonates, micro-environment, fabric, isotope geochemistry, alteration, primary fabric

1. Introduction: non-marine carbonates and early diagenesis?

Non-marine carbonate depositional environments, facies distributions, fabrics and geochemical signatures have been under the spotlight over the past decade (Pentecost, 2005; Fairchild et al., 2006; Alonso-Zarza and Tanner, 2010a; Pedley and Rogerson, 2010; Brasier, 2011; Capezzuoli et al., 2014). This is in part because they form important continental paleoclimate archives (Andrews, 2006; Fairchild et al., 2006; Fairchild and Treble, 2009; Tanner, 2010; Frantz et al., 2014). Further, several non-marine carbonate fabrics have been recognized in subsurface lithologies of economic interest (Harris, 2000; Della Porta, 2015; Wright and Barnett, 2015; Schroeder et al., 2016; Claes et al., 2017a; Mercedes-Martín et al., 2017). Furthermore, many carbonate factories in non-marine environments have been studied to understand close interactions between micro- and macrobiota (bacteria, algae, bryophytes, plants) that influence mineral precipitation processes, pore fluids and the resulting carbonate fabric (Freytet and Verrecchia, 1998; Benzerara et al., 2006; Bissett et al., 2008; Takashima and Kano, 2008; Bontognali et al., 2010; Jones, 2010; Peng and Jones, 2013; Pace et al., 2016). Because diagenesis of non-marine carbonate rocks is commonly apparent, it is surprising that studies addressing the nature, distribution, processes and controls on early diagenesis of terrestrial

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carbonates are rather scarce (Folk and Assereto, 1976; Kendall and Iannace, 2001; Golubić et al., 2008; Armenteros, 2010; Frisia, 2015). This contrasts with an extensive body of literature on diagenesis of marine sediments. Diagenesis in these continental environments often starts early, from fluids closely resembling those responsible for carbonate formation, and it never really stops. This is the inescapable conclusion from many studies of field sites and experiments, as discussed here. As these early diagenetic processes and products have so far only been tangentially addressed in continental settings, their variety and impact on geochemical and geochronological proxies are far from fully understood.

This review summarizes and integrates recent insights and emerging approaches to studying early diagenesis, leading to the presentation of a conceptual scheme to address these processes in non-marine carbonates. Burial digenesis (deeper than the immediate subsurface) is not included here. For that the reader is referred to several authoritative reviews on the subject (Tucker and Wright, 1990; Flügel, 2004; Armenteros, 2010; Moore and Wade, 2013; James and Jones, 2015).

We define ‘non-marine carbonates’ as carbonate rock deposits that form and may be syn-depositionally transformed (“diagenetically altered”) under the strong influence of meteoric waters, including situations with various degrees of mixing with seawater, evaporative or basinal fluids (Fig. 1, 2). Non-marine carbonates are primarily located in continental settings, with some on islands (Benzerara et al., 2010; Kremer et al., 2012). The following deposits are included in this review under the heading non-marine carbonates (Fig. 1); (1) karst and cave deposits, (2) hot and cool spring and stream carbonates, (3) calcretes and (4) marginal, lacustrine-palustrine carbonates, including abiogenic, microbial and biogenic deposits (Table 1). There is a continuum in space and time between these different environments and their rock products such that they are most easily addressed together under a collective heading (Freytet and Plaziat, 1982; Alonso-Zarza, 2003; Brasier, 2011; Della Porta, 2015). A limited number of reference examples that cover this spectrum is selected, with less focus on biogenic carbonate deposits such as ostracod, gastropod, bivalve beds, to illustrate

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common early diagenetic processes in these deposits and environments (Fig. 1, Table 1), which are the focus of this review.

Most research has been published on Recent to Quaternary deposits. Non-marine carbonates have been recognized and reported from deposits as old as the late Archaean and Palaeoproterozoic (for review see Brasier, 2011). Amongst the most ancient deposits are examples of lacustrine, pedogenic and hydrothermal spring carbonates (Watanabe et al., 2000; Melezhik and Fallick, 2001; Bolhar and Van Kranendonk, 2007; Awramik and Buchheim, 2009; Fairchild et al., 2016). Given the focus here on the early (syn-depositional) stages of diagenesis, the examples most often used here range between Miocene and Recent in age (Table 1), with a strong emphasis on Quaternary deposits.

2. Defining and describing early diagenesis: the conundrum in non-marine carbonates

'Diagenesis' refers to a suite of 'post-depositional' processes that has an important impact on chemical, mechanical and petrophysical properties of carbonate sediments (Bathurst, 1975; Berner, 1980; Moore and Wade, 2013) as well as on the preservation of depositional fabrics, (micro)biological assemblages, geochemical and geochronological signatures.

One classic scheme to classify diagenetic processes affecting *marine* carbonate rocks starts from the concept of diagenetic environments or 'realms'; these are 'surface or subsurface zones typified by specific processes which result in predictable and similar patterns of diagenesis that can be studied in thin sections and by geochemical methods' (Flügel, 2004). Around typical marine carbonate systems like coral reefs, three major realms may be recognized (Choquette and Pray, 1970); (i) the near-surface zone, characterized by phreatic conditions and normal or modified (marine) pore fluids (*eogenetic* zone), (ii) a near-surface zone resulting from, the exposure of sediments to subaerial conditions and meteoric vadose or phreatic conditions (*telogenetic* zone), and (iii) the subsurface burial realm where pore fluids are often a mixture of modified meteoric, marine waters or chemically complex brines as a result of long-lasting water-rock interactions (*mesogenetic* zone) (Moore, 2002).

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This subdivision was practical for marine carbonate fabric description, including porosity characteristics but is no longer widely used. An alternative, recent approach involves subdivision based on the dominant fluid or fluid mixtures present (Flügel, 2004; Moore and Wade, 2013; Swart, 2015); this may be freshwater, marine, mixed marine-meteoric and subsurface, or burial, diagenetic fluids (Fig. 2). In this view, water chemistry, flux, temperature and pressure of rock-water interaction 'drive diagenetic processes' (Moore and Wade, 2013).

Neither of these approaches suits early non-marine carbonate diagenesis. Descriptions of processes in the meteoric, vadose and phreatic zone focus solely on the corrosion capacities of dilute, fresh waters, and limited cementation, affecting previously deposited and uplifted carbonate sediments (Longman, 1980; Meyers and Lohmann, 1985; Armenteros, 2010; Moore and Wade, 2013). Diagenesis of non-marine carbonates is, furthermore, not always driven by low ionic strength meteoric waters, as illustrated in Figure 2. It is something of an oversight that the range of early diagenetic conditions (fluid composition, temperature, biology) and processes were nearly absent from classical carbonate rock diagenesis frameworks. The majority of non-marine carbonate deposits nucleate and precipitate from solution – or to a lesser extent – result from biogenic secretion. This makes the end of primary deposition and start of diagenesis hard to pinpoint. Most researchers recognize this, but few address it explicitly. Renaut and Jones (1997) mentioned that "all calcite precipitated directly from spring water is considered formational, whereas biogenic or abiogenic alteration is considered diagenetic". In practical terms, this definition is hard, if not impossible, to apply. Pentecost (2005) working on travertine systems tackles the dilemma by defining the primary fabric" as that present at the active travertine surface (including the top 1mm of deposit)". However, this is also problematic because 'primary' crystal nucleation and growth frequently happen below 1 mm sediment depth in non-marine carbonate environments. For our purposes, crystalline carbonate precipitates and carbonate deposits that formed at or along the initial, depositional surface from primary pore fluids can be considered to make up the primary fabric. In this context, 'early

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diagenesis' refers to those rock fabric altering processes and transformations that take place or start during and just after deposition.

2.1 Summary of non-marine carbonate fabrics, mineralogy and processes of crystal formation

2.1.1 Fabrics and mineralogy

Presumed primary depositional fabrics of non-marine carbonates have been rather extensively covered in several recent reviews (Alonso-Zarza, 2003; Fairchild et al., 2006; Brasier, 2011; Gandin and Capezzuoli, 2014; Della Porta, 2015; Frisia, 2015; Zamanian et al., 2016) and volumes (Pentecost, 2005; Alonso-Zarza and Tanner, 2010a; Pedley and Rogerson, 2010; Fairchild and Baker, 2012), as well as in an increasing number of individual case studies. Table A1 therefore summarizes a number of these micro- to macrofabrics as observed in the field and under transmitted light microscopy, plus key literature that offers an overview of the range of commonly reported 'primary' carbonate products. In many of these cases, the presence and potential influence of (early) diagenetic processes on the fabrics is not explicitly addressed.

Table A2 provides a summary, including references from field and laboratory studies, of several common carbonate mineralogies in non-marine carbonates. The initial mineralogy is important as it will influence its reactivity and the so-called 'diagenetic potential'. Not all parameters controlling the occurrence of one or the other mineralogy or polymorph are yet fully resolved though (Renaut and Jones, 1997; Kele et al., 2008; Wassenburg et al., 2012; Riechelmann et al., 2014; Jones, 2017) and this may in part be related to pathways and molecular-scale controls on crystal formation that are only recently being unveiled and addressed.

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2.1.2 Recent insights into crystal formation through transient precursor phases

High-resolution microscopic (cryo-SEM, -TEM) and experimental observations now exist that demonstrate that processes of crystal nucleation and growth are more diverse than the conventional model of monomer-by-monomer addition of chemical species (atom, ion, molecule). New pathways are found to involve particle attachment and a range of transient, amorphous, 'precursor' phases (Radha et al., 2010; De Yoreo et al., 2015; Purgstaller et al., 2016; Rodriguez-Blanco et al., 2017; van Driessche et al., 2017).

The implications of newly discovered nano-scale crystallization processes on carbonate stability domains, and on the exact $CaCO_3$ polymorph that forms, plus the fabrics and geochemical signatures of minerals used in environmental studies, requires further study and quantification (Sánchez-Román et al., 2011; Demény et al., 2016; Rodriguez-Blanco et al., 2017). Transformation from amorphous calcium carbonate (ACC) to intermediate metastable phases, for example, appears to be a very rapid, often multistage, reaction process taking seconds or minutes to hours, during which stable crystalline products and metastable phases may co-exist (Rodriguez-Blanco et al., 2011, 2012, 2017; Bots et al., 2012; Zhang et al., 2012; Nielsen et al., 2014). Lab and field studies report ACC phases found in close association with crystalline $CaCO_3$ (Jones and Peng, 2012a; Pedley, 2014) and/or organisms (cyanobacteria) or organic substances (Couradeau et al., 2012; Benzerara et al., 2014; Martignier et al., 2017). The transformation from ACC to crystalline carbonate mineral is commonly suggested to be associated with an ACC dehydration-step (Rodriguez-Blanco et al., 2011; Bots et al., 2012; Demichelis et al., 2014; De Yoreo et al., 2015), but the mechanism seems to be influenced by, amongst others, temperature, solution pH, Mg:Ca ratios, sulphate concentrations and organic matter (Rodriguez-Blanco et al., 2012; Zhang et al., 2012; Purgstaller et al., 2016). Micro-environmental effects are evidently important for these nano-scale phase changes.

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2.2 Early diagenesis and the role of the micro-environment

With modern techniques, one can look at increasingly smaller scales, down to and beyond the nanometer level (Pace et al., 2016). Current research has demonstrated the tight interaction between very early (syn-depositional) carbonate recrystallisation and changes in associated non-carbonate phases, including (microbial) organic matter, Ca-oxalates and clay minerals. These processes typically take place in 'micro-scale environments' or 'niches' within primary pore spaces and biofilms. Here we highlight at a few such processes, though there are many others in nature.

2.2.1 Ca-oxalates and their transformation into carbonate phases.

Calcium oxalates are extremely common in nature, and are particularly linked with fungi, lichens and vascular plants (de Bary, 1887; Simkiss and Wilbur, 1989; Horner and Wagner, 1995; Verrecchia et al., 2006). They come in various hydration states, i.e. as a monohydrate (whewellite, $CaC_2O_4.H_2O$) or as polyhydrates (collectively as weddellite, $CaC_2O_4.nH_2O$, $2 \leq n \leq 3$). Dehydration rapidly causes weddellite to transform to whewellite. Graustein et al. (1977) reported that weddellite found in soils of New Mexico had dehydrated to whewellite by the time it was measured in the laboratory.

Because of the abundance of calcium oxalates and calcium oxalate producing organisms it is somewhat surprising that there have been relatively few studies linking calcium oxalate deposition with calcium carbonate production. This may in part be due to the similar elemental composition of calcite, whewellite and wedellite, such that structures identified as comprising Ca, C and O are assumed to be $CaCO_3$. This challenge was tackled by Verrecchia et al. (1993) with a windowless Energy Dispersive Spectrometer (EDS) detector attached to an SEM that allowed comparison of the relative amounts of C in crystals, and thus distinction between calcium oxalates and carbonates. Many modern EDS detectors are able to measure relative abundances of light elements including carbon without having to remove the window, so this technique is now widely accessible. Verrecchia et al. (1993) used this approach to distinguish crystals of calcite from crystals of calcium oxalate in

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'Needle Fibre Calcite' (NFC). This common fungal hyphae-related fabric (Wright, 1986; Verrecchia and Verrecchia, 1994), best observed by SEM and reviewed by Verrecchia and Verrecchia (1994), and updated by Cailleau et al. (2009), consists of elongated crystals measuring tens to hundreds of microns in length and a few microns in width. Crystals may be randomly stacked, or form parallel clusters, aggregates or networks (Fig. 3A). Their exact biotic or abiotic origin, however, remains debated (Martín-Pérez and Košir, 2017). Verrecchia et al. (1993) showed that short crystals and spikes surrounding the exterior of the calcified fungal filaments they found in some Quaternary calcretes of Israel had compositions better compatible with calcium oxalates than with calcite. They also showed that most needles and mineral encrusted fungal hyphal walls had intermediate compositions between calcite and calcium oxalate.

Verrecchia et al. (1993) envisaged that transformation of calcium oxalate to calcite was bacterially mediated, following hypotheses of Cromack et al. (1977) and Philips et al. (1987). Experiments have since shown that some soil bacteria (including *Ralstonia eutropha* and *Xanthobacter autotrophicus)* degrade oxalates, using them as a carbon and energy source, resulting in production of carbonic acid and ultimately carbonate ions that can react with locally sourced calcium to produce calcite or vaterite (Braissant et al., 2002). This oxalate oxidation locally raises the pH (Braissant et al., 2002, 2004), which aides carbonate mineral precipitation and growth in otherwise low pH soils (Cailleau et al., 2011). Calcium oxalates produced by Iroko trees of Ivory Coast (Cailleau et al., 2004) and Cameroon (Cailleau et al., 2011) are known to be converted into voluminous accumulations of calcium carbonate in otherwise low pH soils. Here the organic 'litter' produced by the trees is initially broken down by organisms including termites and fungi, releasing the calcium oxalates so that they can be processed by the oxalotrophic bacteria.

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2.2.2 The role of microorganisms and organic matter in carbonate crystal formation

Mostly based on in-vitro laboratory experiments, recent advances have been made in unraveling the different, microbial-related and organic matter (degradation) processes that facilitate and localize carbonate crystal formation, and how they can potentially be driven, e.g. for biotechnical purposes (Zhu and Dittrich, 2016). These processes fall roughly into two categories; microbial carbonate precipitation (1) as a by-product of common metabolic activities like oxygenic/anoxygenic photosynthesis, aerobic respiration, denitrification, ammonification, sulfate reduction, methanotrophy, iron reduction (Michaelis et al., 2002; Dupraz et al., 2004, 2009; Visscher and Stolz, 2005; Rogerson et al., 2014; Zhu and Dittrich, 2016); and (2) by using by cell walls, filamentous structures or extracellular organic matter (EOM) (including extracellular polymeric substances (EPS) and low-molecular weight organic carbon) (Decho et al., 2005) as templates for crystals with different habits (Shiraishi et al., 2008; Dupraz et al., 2009; Arp et al., 2010; Pedley, 2014; Rogerson et al., 2014; Fig. 3B, C). These surfaces may provide a particular micro-environment by their negatively charged functional groups (such as carboxyl, amine, phosphate and hydroxyl groups) that trap or release divalent cations (Ca^{2+}, Mg^{2+}), thereby affecting their concentration in solution (Dupraz and Visscher, 2005; Visscher and Stolz, 2005; Dupraz et al., 2009; Arp et al., 2010; Roberts et al., 2013; Zhu and Dittrich, 2016). They may as well glue particles together, such as certain filamentous microbes in caves, or retain water in their framework (Barton et al., 2001; Barton and Northup, 2007; Jones, 2010).

Microbial activity in micro-niches also encourages processes at the cell wall-pore fluid interface during early diagenesis. This is especially found in association with the degradation and alteration of organic matter (e.g. by sulphate reduction), just below active microbial mats when divalent cations are very locally released (Dupraz et al., 2009; Rogerson et al., 2014; Pace et al., 2016). Secondary carbonate precipitation may occur as a result, sometimes as the expense of primary unstable and/or amorphous phases. Experimenting with microbial isolates from Altarmira cave in Spain, Sanchez-Moral et al. (2003) demonstrated that metastable phases such as vaterite and/or monohydrocalcite

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formed first. Such metastable and/or amorphous phases can be easily transformed into calcite phases through early diagenetic processes.

Arp et al. (2003) added to these findings. They demonstrated that microbialites in Satonda Crater lake (Indonesia) were formed through passive and diffusion-controlled EPS-mediated permineralization of the biofilm mucus at the contact with the lake water, resulting in micropeloidal aragonite clots. Fibrous aragonite cements grew into exopolymer pore spaces and voids. However, in contrast to extreme soda lakes where EPS degradation supports carbonate precipitation, the aragonite precipitation at Satonda results from changes in the carbonate equilibrium driven by seasonal mixing of mixolimnion with monimolimnion waters, and subsequent CO_2-degassing. The Arp et al. (2003) study demonstrates that besides the degradation and alteration of organic matter, extrinsic environmental conditions may govern early diagenetic precipitation.

2.2.3 The role of Mg-silicates in secondary carbonate formation

Warren (2016) emphasizes that the magnitude of detrital clastic input cannot be neglected in marginal lacustrine and palustrine areas and that clay authigenesis in evaporitic basins is favoured through the transformation of precursor clays. Episodic surface inflow and groundwater discharge influence pH, pCO_2, Mg/Si and the salinity of the fluids resulting in the precipitation of kerolite, stevensite, sepiolite, palygorskite, hectorite or saponite (Warren, 2016). Furthermore, authigenic clay minerals enriched in Mg form in recent, hypersaline lacustrine and palustrine settings with high pH, as early evaporative precipitates (Eugster and Jones, 1979; Fisher, 1988; Calvo et al., 1999), where they occur in close association with carbonates (Calvo et al., 1995; Freytet and Verrecchia, 2002; Arp et al., 2003; Kremer et al., 2012; Burne et al., 2014; Tosca and Masterson, 2014; Pace et al., 2016).

Experimental studies have shown that the formation of Mg-silicates from a primary solution evolves through poorly crystalline intermediates (Jones, 1986; Tosca et al., 2011). Tosca and Masterson

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(2014) have proven that the loss of interlayer sites and surface hydration are important processes driving poorly crystalline phases (Mg-silicate ‘gels’) to change into crystalline Mg-silicate minerals. Initial Mg-silica precipitation may change the brine fluids such as by depletion of Mg over time, lowering the Mg:Ca ratio of the precipitating fluids and as such favoring low Mg-calcite precipitation (Wright and Barnett, 2015; Wright and Tosca, 2016). This model might explain the occurrence of both carbonates and Mg-silicates (Fig. 3D) in, for example, highly alkaline lake settings such as the Aptian Barra Velha Formation (Santos Basin, offshore Brazil; Wright and Tosca, 2016).

Further poorly crystallized Mg-silicates are now also often found and recognized in association with EOM and microbial cell walls (Arp et al., 2003; Bontognali et al., 2010, 2014; Kremer et al., 2012; Burne et al., 2014; Zeyen et al., 2015). In these cases, and tightly associated to the processes outlined in section 2.2.1, they may play a role in the formation, transformation and replacement of metastable carbonate phases. Burne et al. (2014) building on Wacey et al. (2010) provided petrographic evidence for stevensite growing around cyanobacterial sheaths and in the alveolar web of thrombolite biofilm EPS in some specimens taken from Lake Clifton (western Australia). Here, diatoms may have acted as a local silica source, binding with Mg from the lake water. In this case, the Mg-silicates gradually entombed the microbial filaments on which they grew and that initially suppressed (by binding cations) the formation of carbonates. Stevensite organomineralization of the biofilm then allowed C and Ca activities to rise in the pore space, and aragonite precipitated.

Pace et al. (2016) similarly reported the nucleation of Mg-Si phases on the EOM in the zone of active oxygenic photosynthesis (pH >10) during the initial stages of microbialite formation in Great Salt Lake (USA). Degradation of EOM by heterotrophs (sulfate reducing bacteria) increases alkalinity and allows the nucleation of aragonite during the first diagenetic phase, followed by partial dissolution in the deepest part of the mat once advanced EOM degradation created a zone of low pH (Pace et al., 2016). In this localized, lowered and fluctuating pH zone, pockets of partially degraded EOM bind

Ca^{2+} from dissolving aragonite and Mg^{2+}, partly derived from the evolving amorphous Mg-Si phase (decreasing Mg:Si ratio). This joined process leads to the precipitation of dolomite at the interface with and at the expense of (replacing) EOM, metastable aragonite and the Mg-Si phase (Pace et al., 2016).

2.3 Neomorphism

Neomorphism (Folk, 1965) refers to all in-situ transformations of one mineral and itself (recrystallisation) or a polymorph (inversion) that generally take place through dissolution-reprecipitation across a very thin film of water. Neomorphism and in particularly aggrading neomorphism is a process frequently reported to affect primary carbonate precipitates in non-marine environments (Pentecost, 2005; Fairchild et al., 2006; Arp et al., 2013a; Peng and Jones, 2013; Martín-García et al., 2014; Frisia, 2015).

Several studies are illustrative concerning the recognition of purported neomorphic fabric changes. Such studies usually integrated observations from recent and ancient deposits at the same locality. This approach can be criticized because there is commonly no definitive proof that the supposedly altered material was actually older than the apparently more pristine rock, though in most cases this seems the only practical approach to tackling early diagenesis. Good examples include Frisia (1996) and Frisia et al. (2002) who showed how aragonitic fan layers composed of needle and ray crystals were progressively replaced by an anhedral, equant-shaped to elongated calcite crystal mosaic in a French speleothem. Similar fabrics, where fibrous or micritized aragonite relicts are encased in anhedral calcite mosaics characterize the Castañar and Basajaún Extea cave deposits (Spain) (Martín-García et al., 2009, 2014) and the process is observed in Recent and Holocene travertine sequences at Mammoth Hot Springs (Yellowstone National Park, USA) (Fouke et al., 2000; Chafetz and Guidry, 2003; Fig. 4 A-C). The relics may preserve the initial mineralogy or be textural relics. In other cases, neomorphism of aragonite may result in a nearly complete destruction of the primary fibrous fabric,

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leading to inclusion-rich elongated, calcite cements (Arp et al., 2013a; Martín-García et al., 2014; Frisia, 2015).

Neomorphism is typically considered as a combined and co-eval dissolution-precipitation process in the presence of a fluid undersaturated with respect to aragonite and saturated for calcite. This may result from short (intra-seasonal) to longer timescale (inter-annual or permanent) modifications of the precipitation conditions or pore fluids (e.g. concentration of CO_2, water discharge, prior precipitating phases) (Domínguez-Villar et al., 2017). Based on SEM and TEM observations, Frisia et al. (2002) suggested that small calcite rhombohedra precipitated initially between the aragonite needles without aragonite dissolution. Those small calcite cement rhombs formed nucleation seeds for calcite growth. The latter took place in parallel with neomorphism of aragonite when the aragonite saturation decreased. TEM observations by Frisia et al. (2002) furthermore suggest that physical crystal defects such as twins, dislocations and surface irregularities in the aragonite can have a control on the location and kinetics of the neomorphic process. Geochemical data (Arp et al., 2013b; Domínguez-Villar et al., 2017) have been used to support hypotheses of partially open systems, with the neomorphic process occurring both along an angstrom-thin dissolution - re-precipitation fluid film and within the larger, intercrystalline pores in exchange with bulk fluid (Arp et al., 2013b).

Observations on cool water spring and stream carbonates led some authors to suggest that (aggrading) neomorphism not only affects metastable phases like aragonite and high-magnesium calcite (inversion), but also calcitic deposits (Fig. 4D) (Wright et al., 1997; Janssen et al., 1999; Arp et al., 2001; Davaud and Girardclos, 2001; Rainey and Jones, 2007). In their ‘neomorphic sequences’, Freytet et al. (1998) and Freytet and Verrecchia (1999), building on previous work by Love and Chafetz (1988), showed a sequence of steps in recrystallization of calcitic, micritic and sparitic envelopes of pro- and eukaryotic filaments. They proposed that micritic envelopes, related to *Schizothrix* colonies, could evolve into ‘giant laminations’ of columnar, radial palisade crystals with

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organic or micritic matter as inclusions outlining primary lamination and textures. This model was partially disputed by Brasier et al. (2011) who pointed out that spar crystals may commonly be primary, and that most crystals grow perpendicular to the surface on which they are nucleated (i.e. here perpendicular to cyanobacterial filaments). While continued crystal growth seems to happen in calcitic spring and stream environments, the production of 'secondary' palisade spar layers requires that the 'primary' nuclei are suitably oriented for this to happen (Brasier et al. 2011).

Neomorphism in particular can rapidly modify the primary fabric and texture. Several authors suggest that biological inclusions present in the active deposits gradually vanish during the formation of continuous, dense calcite crusts (Janssen et al., 1999; Arp et al., 2001; Peng and Jones, 2013). Processes of neomorphism in terrestrial carbonate rocks are poorly understood, but reportedly affect micritic, microsparitic, and sparitic precipitates of variable mineralogy. Neomorphism is commonly inferred – rightly or wrongly - where rocks exhibit calcitic, coarsely crystalline mosaic fabrics, often consisting of anhedral-subhedral equant (sparry) calcite (Rainey and Jones, 2007), or columnar calcite crystals (Love and Chafetz, 1988) or radial palisade calcite with sweeping extinction (Freytet and Verrecchia, 1999; Pache et al., 2001; Golubić et al., 2008).

2.4 Cementation and cements

Cementation is the precipitation and growth of crystals in pores of an existing fabric thereby decreasing the pore space (Flügel, 2004). Early cements may form from waters that infiltrate, percolate or rise through the porous fabric and from water held in isolated voids. Cementation in relation to meteoric fluids has classically been placed and discussed in two different hydrological zones, the *vadose* zone above the water table with both water and air in pores, and the *phreatic zone* where pore spaces are saturated with water (freshwater, water of mixed composition, saline waters) (Fig. 2; Longman, 1980). Those zones are dynamic and may move position vertically and laterally depending on the water table (Moore and Wade, 2013). The cementation phenomena associated

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with them, including microstalactitic and meniscus fabrics (vadose zone; Fig. 5A) and pore-filling circumgranular, drusy and epitaxial cements (phreatic zone), have been well covered in numerous overview and case study works (Moore and Wade, 2013; James and Jones, 2015).

Cement fabrics observed in several terrestrial case studies (Table 1) are, however, more diverse and often show crystal textures commonly described from the marine realm. They consist of composite blocky, platy or spar calcite crystal (Fig. 5B; Chafetz and Guidry, 2003; Turner and Jones, 2005; Rainey and Jones, 2007; Jones and Renaut, 2008; Arp et al., 2013b), columnar, acicular, gothic arch or bladed crystals forming isopachous calcite (Fig. 5C, D) and fibrous aragonite void lining cements (Chafetz et al., 1994; Arp et al., 1998; Claes et al., 2015), radial splays (Barth and Chafetz, 2015), anhedral calcite-micrite banded crusts, mosaic cements and overgrowths of small trigonal prisms or former aragonite needles (Fig. 5E) (Rainey and Jones, 2007; Jones and Renaut, 2008; Gandin and Capezzuoli, 2014; Claes et al., 2015). How these cement types relate to saturation state, flow, water composition (Mg/Ca) and the presence of organisms may follow similar trends to those summarized by Flügel (2004).

Cements can be found in interparticular, intercrystalline or framework primary pores or as calcite mosaics filling small, secondary cracks. When the host fabric is not fully lithified yet, a displacive fabric may develop, resulting in floating grains in, for example, calcretes (Armenteros, 2010). Gandin and Capezzuoli (2014) furthermore reported of geodic cements (Fig. 5F) consisting of rims of gothic arch, trigonal and euhedral calcite crystals and linked them to the evaporation of residual, oversaturated fluids that had been trapped within the primary pore space of e.g. mineralized microbial mat laminae in fossil, Italian hot spring deposits. Similarly, Arp et al. (1998) report of fibrous and botryoidal aragonite crystals that line water-filled lenticular shrinkage voids and gas bubbles within a partly lithified microbial mat.

To distinguish cements petrographically from any primary crystal precipitate or encrustation can be challenging in many non-marine carbonates (Chafetz and Guidry, 2003; Pentecost, 2005; Rainey and

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Jones, 2007; Jones and Renaut, 2008; Martín-Pérez et al., 2015a). In spring carbonates and speleothems, precipitation, neomorphism (inversion and recrystallization) and cementation are typically a continuum (Fig. 4A, 5C) and may take place contemporaneously, at different depths (Martín-García et al., 2014), or these processes may alternate in step with water chemistry changes (Frisia et al., 2002; Jones and Renaut, 2010). This furthermore means that otherwise 'primary' surface deposits, e.g. travertines, can also develop as 'cements' in cavities of existing non-marine carbonates (Rainey and Jones, 2007), like microbial build-ups, as for example in the Green River Formation (Seard et al., 2013). Where primary precipitation, neomorphism and cementation happen simultaneously, the waters from which initial precipitates form also mediate the first steps of early diagenesis. This means the 'original' and 'diagenetic' water geochemical signals may be indistinguishable (Andrews, 2006).

2.5 Bio-erosion and micritisation

A further set of processes having a degrading effect on initial, crystal substrates results from the action of organisms and/or presence of organic matter. Schneider and Le Campion-Alsumard (1999) demonstrates the importance of biological corrosion (defined as dissolution of carbonate substrata by secreted acidic substances) and biological abrasion (mechanical removal of carbonate surfaces by grazing organisms), both defined as bio-erosion, by endolithic cyanobacteria and lichens in micro-niches and/or micro-karst. The dissolved and particulate bioerosion products can be transported and deposited in subsequent sedimentary cycles. Experiments have proven the importance and complexity of fungally induced substrate dissolution, micritization and demicritization, but also grain-to-grain bridging, cementation and replacement (Verrecchia, 2000; Kolo et al., 2007).

Sparmicritisation (Kahle, 1977), as a particular process, is well-known in marine sediments, and in lakes (Armenteros, 2010), resulting in micrite envelopes of allochems (Bathurst, 1975; Flügel, 2004). A similar process, mediated by the activity of cyano- and other bacteria, fungi and algae can

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transform spar, columnar or fibrous crystals to micrite or microspar in non-marine settings (Fig. 5G) (Chafetz et al., 1994; Jones, 2010; Capezzuoli et al., 2014). Microorganisms, colonizing the surface during periods of reduced precipitation rates (Takashima and Kano, 2008), or present as endolithic communities in porous laminae of a primary crust, are believed to break apart crystals (Fig. 5H) by their boring activity. This process can be accelerated by etching from (heterotrophic) bacterial decomposition of organic matter and the dissolution/breaking apart of partly indurated crystals (Arp et al., 2001; Jones, 2010; Jones and Peng, 2012b). The effect of biogenic spar micritization is expected to decrease - or change - with depth as light becomes limiting for phototrophic organisms and the dominant microbial community will change or cease activity (Jones, 2010).

Further, in caves, the process of micritisation has often been reported as ‘condensation corrosion’ (Martín-García et al., 2011, 2014; Martín-Pérez et al., 2012). During a hiatus in crystal growth, or along small inter- and intracrystalline pores and discontinuities, acidic atmospheric water condenses on and dissolves the speleothem surface.

Micritisation has been held responsible for increasing homogenization of primary shrubs surrounded by calcite spar in Quaternary travertine deposits (Guo and Riding, 1994) and for repetitive microporous, micritic to microsparitic (4 – 10 µm grains) bands or coatings in aragonitic and calcitic speleothems (Martín-García et al., 2009, 2011, 2014). When no ghosts of a primary fabric can be recognized, together with remnants of calcified filaments or endoliths, the mottled micritic fabric can become mistaken for primary micrite laminae.

2.6 Other early diagenetic processes

A series of additional, diagenetic processes are known to operate soon after deposition. They have been well covered in literature (James and Choquette, 1984; Tucker and Wright, 1990; Armenteros, 2010; Moore and Wade, 2013; James and Jones, 2015) and will only be addressed briefly.

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2.6.1 Replacement of other minerals

Non-marine carbonate deposits can be subject to replacement processes when the ground- and pore water chemistry and conditions change. Some examples on the nano- to micron-scale were given in section 2.2. One particular replacement process is the transformation of ikaite to calcite (Suess et al., 1982). Ikaite is only metastable at the Earth's surface and is deposited from phosphate-rich waters at temperatures below 6-7° C (Hu et al., 2014; Sánchez-Pastor et al., 2016) (Table A2) transforming to calcite within 5 hours at temperatures of 10° C, and even more rapidly to calcite via vaterite at temperatures around 20° C (Sánchez-Pastor et al., 2016). Conditions of primary ikaite formation in natural and experimental lab conditions are summarized in Table A2. Calcitic pseudomorphs after ikaite ($CaCO_3.6H_2O$) are known from recent and ancient lakes (Bischoff et al., 1993; Fairchild et al., 2016), streams (Boch et al., 2015) and caves (Field et al., 2017), and have local names including glendonite (Whiticar and Suess, 1998) and thinolite (Shearman et al., 1989; Bischoff et al., 1993; Council and Bennett, 1993). These are recognised by their crystal morphology, ikaite being monoclinic. The transformation from ikaite to calcite involves a 68% volume decrease (Shaikh and Shearman, 1986). Consequently, the final rock products are typically porous, and can be readily recognised (Fig. 6A).

Some other common, important replacement processes are dolomitisation and silicification. Early diagenetic replacement of $CaCO_3$ or silicate minerals by Mg-carbonates or poorly ordered dolomite, $CaMg(CO_3)_2$, is associated with evaporative saline waters, lowered sulphate concentrations and elevated Mg/Ca ratios (Fig. 6B, C) (Table A2). Early dolomitisation processes often yield non-stoichiometric and poorly ordered Mg-rich carbonates (Bontognali et al., 2014; Gregg et al., 2015). Much has been published and discussed on a variety of dolomitisation models (Machel, 2004). In non-marine depositional environments, early diagenetic dolomitization may follow the sabhka playa model (Vasconcelos and McKenzie, 1997) where evaporation and hypersaline conditions create Mg-rich, dense fluids that sink. This is a process invoked in marginal lacustrine and palustrine settings (Fig. 6B, C) and in calcretes, thereby forming 'dolocretes' (Armenteros, 2010; Bontognali et al., 2010;

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Richter et al., 2014). Arp (1995) invoked a mixing zone model for the dolomitisation of high-magnesium calcite deposits in the case of the Ries Crater algal bioherms. Petrography and geochemistry suggested phreatic pore water within the lake margin bioherms fluctuated through time, causing mixing of low ionic strength meteoric waters with saline lake water within the pore space. Such dolomitization models are however much debated and contested when it comes to explaining large-scale dolomitisation phenomena (Hardie, 1987).

Though dolomite is more rarely present in cave deposits, it has been reported as a replacement product of metastable, hydrous phases (hydromagnesite, huntite) (Sánchez-Román et al., 2011; Martín-Pérez et al., 2012, 2015a) and as a product of dolomitization in relation to the alteration of $CaCO_3$ in contact with Mg-rich fluids (Alonso-Zarza and Martín-Pérez, 2008). Mg-enrichment of speleothem-depositing fluids occurs through dissolution of adjacent dolostone lithologies, followed by fluid evaporation and the progressive crystallization of Ca-rich minerals, leaving the residual fluid enriched in Mg. Mg-rich carbonates have been reported as forming microcrystalline to coarse, fan-shaped and spheroidal crystals that cover aragonite textures, partly replacing the precursor $CaCO_3$ phase (Fig.6D; Martín-Pérez et al., 2012, 2015a).

Early diagenetic replacement of carbonate by silica is favored in conditions where a silica-charged fluid is available (>6 mg L^{-1} SiO_2) and both pH (~6 to >9) and temperature are strongly fluctuating (Fig. 6 B, C), thereby affecting carbonate and silica solubility (Bustillo, 2010). Such conditions are found where, for example, pCO_2 varies, like in cave atmospheres (Woo et al., 2008), or where waters of different composition and saturation state mix (saline/alkaline, meteoric waters), or where ascending, Si-bearing thermal waters cool down. Combined carbonate precipitation and early diagenetic silica precipitation and replacement can imply water chemistry fluctuations during deposition (Bustillo, 2010). The dissolved silica can be sourced from associated or extra-formational clays, volcanic or metamorphic rocks, or even siliceous microorganisms like diatoms within the deposits (Bustillo et al., 2002; Burne et al., 2014). Silica often first forms as metastable opal A,

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transforming to opal CT and then quartz, or may form directly as stable quartz (Armenteros et al., 1995; Bustillo et al., 2002). Early, pseudomorphic silicification may protect primary features from later, burial- or subaerial exposure-related alteration and dissolution. As such, silicified parts of non-marine carbonate sequences can still hold important clues to primary circumstances of non-marine deposition (Knoll et al., 2013). Silica replacement of evaporites ($CaSO_4$), for example in sabhka settings, has been commonly reported and the reader is referred to Warren (2016) for a full review of replacement processes (Folk and Pittmann, 1971), the (biogenic) silica sources and resulting fabrics.

2.6.2 Dissolution

Local-scale dissolution is involved in processes like neomorphism and replacement, but the dilute composition of meteoric and freshwater may also lead to a more pervasive dissolution phase of mineral components (Moore and Wade, 2013), resulting in pore enlargement (vugs) (Fig. 7A), karstification (Fig. 7B) and cavern development. Meteoric dissolution can be held responsible for enlarged, vuggy porosity and truncation of primary features observed on a microscopic scale (Chafetz and Guidry, 2003; Rainey and Jones, 2007). Episodes of dissolution or etching upon exhumation can be subtle and recurrent, contributing to banded or layered dendrite and calcite fan crystal deposits (Jones and Peng, 2012b; Brasier et al., 2015). In some cases, detailed epifluorescence or optical cathodoluminescence petrography might be needed to decipher dissolution phases between periods of precipitation or cementation (Rainey and Jones, 2007; Fig. 7C).

2.6.3 Mechanical weathering

Other, early, physical alteration processes may take place upon subaerial exhumation like desiccation (Fig. 7D, E), brecciation and shrinkage in, for example, calcretes, in microbial mats, lacustrine carbonate muds or dry ephemeral ponds (Fig. 7F; Arp et al., 1998; Freytet and Verrecchia, 2002;

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Brasier, 2011; Gandin and Capezzuoli, 2014). Resulting fabrics like in-situ formed pseudobreccias, horizontal and vertical cracks and teepee formation can also result from root activity, thermal and moisture related expansion and contraction or crystallization in pores upon evaporation (Eren, 2007; James and Jones, 2015). Breaking up of deposits may furthermore facilitate mechanical transport and sediment re-deposition.

3. Impact of early diagenesis on carbon-, oxygen- and clumped isotope records and paleoenvironmental interpretations

3.1 Stable carbon and oxygen isotopes in non-marine carbonates

Figure 8 shows a compilation of carbon and oxygen stable isotopic compositions of carbonate sediments from the selected reference cases introduced in Table 1. An overview of carbonate stable isotopic compositions characteristic of vadose and phreatic, meteoric diagenesis can be found in in several publications and books (Allan and Matthews, 1982; Morse and Mackenzie, 1990; Hoefs, 2004; Sharp, 2007; van Dongen et al., 2007; Moore and Wade, 2013; Swart, 2015). Several processes and trends are indicated in Figure 8.

The range of stable isotopic signatures is wide (Fig. 8) (Allan and Matthews, 1982; Özkul et al. ,2013; Della Porta, 2015; Deocampo, 2010; Pentecost, 2005). It varies strongly with spatial and temporal changes in environmental conditions (temperature, rainfall, evaporation, hydrology) and fluid composition (Fig. 2), but also in relation to strong physicochemical and biological gradients along flow paths (cooling/heating, evaporation, CO_2 degassing - or ingassing, respiration or photosynthesis) (Fig. 8; Fouke et al., 2000; Pache et al., 2001; Andrews, 2006; Fairchild et al., 2006; Alonso-Zarza and Tanner, 2010b; Kele et al., 2011; Arp et al., 2013b; Frantz et al., 2014; Rogerson et al., 2017).

The oxygen isotopic composition of carbonate minerals is controlled by the $\delta^{18}O$ value of the precipitating fluid, the temperature of formation and the carbonate mineralogy besides the pH of

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solution (Rozanski et al., 1993; Zeebe and Wolf-Gladrow, 2001; Dietzel et al., 2009; Affek and Zaarur, 2014; Swart, 2015). In-situ monitoring and data from natural samples demonstrate off-sets as a result of metabolic (Andrews et al., 2004) or kinetic effects during non-equilibrium precipitation in relation to e.g. precipitation rate variations, a process very common in several non-marine carbonate depositional settings such as caves and springs (Coplen, 2007; Dietzel et al., 2009; Kele et al., 2011, 2015; Gabitov et al., 2012; Riechelmann et al., 2013; Kluge et al., 2014; Watkins et al., 2014). Carbon isotopic compositions relate to the available Dissolved Inorganic Carbon (DIC) source (Fig. 8), carbonate mineralogy (e.g. aragonite versus calcite, Tarutani et al., 1969; Romanek et al., 1992; Patterson et al., 1993; Thorrold et al., 1997; White et al., 1999; Böhm et al., 2000; Lécuyer et al., 2004) and to kinetic effects due to fast degassing and high precipitation rates or in-stream biological activity, organic matter degradation (Andrews and Riding, 2000; Fouke et al., 2000; Andrews, 2006), pH and temperature of precipitation (Deocampo, 2010; Swart, 2015). Carbon and oxygen stable isotope signatures can thus be valuable archives of paleoenvironmental, and -climatic variations (Fig. 8) with seasonal, annual or decadal resolution (Fairchild et al., 2006; Kawai et al., 2009; Tanner, 2010; Renaut et al., 2013; Frantz et al., 2014), especially when records of different deposits (e.g. spring carbonates, speleothems besides tree rings, pollen) in the same region can be combined.

3.2 The effect of early diagenesis on $\delta^{13}C$ - $\delta^{18}O$ records

The effect of early diagenetic processes on stable and radiogenic isotope and trace element geochemical signals in non-marine paleoclimatic carbonate records remains a critical, though delicate, point (Andrews, 2006; Fairchild et al., 2006; Martín-García et al., 2009; Milliere et al., 2011; Millière et al., 2011; Wassenburg et al., 2012; Zhang et al., 2014). Only seldom the effect of a single diagenetic process on different stable and radiogenic isotope and trace elemental proxies is, however, investigated in field samples or lab precipitates (Martín-García et al., 2009; Domínguez-

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Villar et al., 2017), nor are the cumulative effects of successive diagenetic transformation processes (Scholz et al., 2014; Ritter et al., 2017).

Most types of continental carbonates are heterogeneous due to the presence of different (diagenetic) cement generations, organic fractions or bioclasts (like ostracods). It is hard to avoid some mixing of the different carbonate phases, even during fabric selective micro-sampling within thin sections to selectively target different carbonate components (e.g. sparite cements, clotted peloidal micrite, crystalline dendrites) (Claes et al., 2015; Della Porta et al., 2017). Nevertheless, in some cases, careful bulk sampling of homogenous parts of carbonate samples can be representative enough to answer the relevant scientific question (Özkul et al., 2013; Toker et al., 2015). Related to the sampling scale is the observation that little information is currently available on the effect of microbial mineralization or the former presence of transient, metastable carbonaceous phases on the geochemical signature in paleoclimatic archives like speleothems (Jones, 2010; Demény et al., 2016).

Fairchild et al. (2006) in a review on the preservation of environmental signals in speleothems points out that where aragonite is inverted to calcite, it is unlikely that original chemical time series can be recovered due to loss and gain of different, chemical species and isotopes (Railsback et al., 2002; Scholz et al., 2014). Detailed studies show that the effect of inversion in cave carbonates on stable carbon and oxygen isotope signals are not unequivocally across different studies and may depend on how far inversion of aragonite to calcite proceeded (Frisia et al., 2002; Martín-García et al., 2009; Zhang et al., 2014). Though, it seems that δ^{13}C values are more conserved than are δ^{18}O values which are more easily reset (Ritter et al., 2017).

Andrews (2006) points out that in studied riverine tufas, it is hard to distinguish when stable carbon and oxygen isotope values may have been affected by a range of diagenetic processes (including cementation, micritisation and aggrading neomorphism). Apparent lack of isotope signal alteration does not necessarily indicate lack of diagenesis, but rather shows that isotopes may not be diagnostic

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(Wassenburg et al., 2012). In their study of Recent precipitates and paleo-riverine tufa deposits, Janssen et al. (1999) remark on a shift in δ^{13}C and δ^{18}O values. For both isotopes they observe that paleodeposits show less variability and a shift towards higher values (<1‰ V-PDB for δ^{18}O; 1.5‰ V-PDB for δ^{13}C). Here we can consider that if early diagenesis is always completed in a short time span, compared to the time scale of interest for paleoenvironmental reconstructions (decadal, centennial, millennial), then isotope geochemical signals preserved in the diagenetic fabric could still be an acceptable reflection of the original depositional conditions (c.f. Brasier et al., 2011). However, if fabric changes happen continuously or intermittently over a longer time, implying that the system has remained open, then a serious overprinting of paleoclimatic and time series information can be expected. Such open system behavior may not only affect – and possibly homogenize - stable isotopic carbonate signatures, but it may also be responsible for observed U/Th offsets and age reversals (Scholz et al., 2014; Claes et al., 2015; Bajo et al., 2016).

3.3 Clumped isotopes in non-marine carbonates

Carbonate clumped isotopes or multiply-substituted isotopologues are isotopologues containing two or more rare isotopes (e.g. ^{13}C and ^{18}O) in one molecule. They have unique thermodynamic properties (e.g. bond vibration frequencies, zero point energies, near-infra-red absorption spectra; Eiler, 2007). Clumped isotopes are reported by the Δ_{47} parameter, which describes the preference of two heavy (rare) isotopes to bind to each other. In geoscience, one of the most important application of clumped isotopes is paleothermometry (Ghosh et al., 2006). Clumping of heavy isotopes (e.g. ^{13}C^{18}O-bonds) relative to stochastic distribution increases with decreasing temperature and vice versa. The blocking or closure temperature of the method is around 250-300 °C where the solid-state exchange ceases (Dennis and Schrag, 2010).

Although the number of clumped isotope studies published during the last several years continues to rise, only a few papers have been published on travertines and tufas to calibrate empirically the

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clumped isotope thermometer in the 6-95 °C temperature range (Kele et al., 2015; Kelson et al., 2017). Speleothems are one of the most important non-marine archives of paleoclimate, where clumped isotope thermometry could be (theoretically) applied with great success. However, speleothems, and also cryogenic cave carbonates, appear to be sensitive to kinetic effects during rapid CO_2 degassing (Affek et al., 2008; Daëron et al., 2011; Eiler, 2011; Wainer et al., 2011; Kluge and Affek, 2012; Affek and Zaarur, 2014; Kluge et al., 2014).

Clumped isotope thermometry can help in constraining conditions of diagenesis in carbonates at temperatures higher or lower than temperature of formation (Swart, 2015) and to reconstruct burial depths and fluid flow history (Huntington et al., 2006; Eiler, 2011; Bergman et al., 2013; Ritter et al., 2017; Sample et al., 2017). With the calculated Δ_{47}-based temperature of formation and using the measured $\delta^{18}O_{carbonate}$ value and the temperature dependence of oxygen isotope fractionation between carbonate and water, the $\delta^{18}O$ of the (burial) diagenetic fluid can be estimated. According to Ferry et al. (2011) clumped isotope thermometry should record the depositional temperature, diagenesis, and recrystallization of carbonate minerals up to at least 100-200 °C, though caution is needed, even at 100°C (Ritter et al., 2017).

So far there have been few studies examining the behaviour of clumped isotopes in well-constrained diagenetic settings (Swart, 2015) and current studies nearly all consider high-temperature alterations. Seldom processes in the early diagenetic realm. Falk et al. (2016) analysed fresh travertine carbonate precipitates from hyperalkaline springs in Oman and found systematic variations in their clumped isotope compositions with formation environments. They suggested that the isotope trends could be applied (1) to identify extinct hyperalkaline springs, (2) to constrain the formation conditions and possible post-depositional alterations, including dissolution and re-precipitation; and (3) to provide information about paleoclimate.

4. Discussion

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4.1 Fabrics and their preservation throughout early diagenesis

4.1.1 What is 'diagenetic' and what is 'primary'?

The result of early diagenetic processes like replacement, neomorphism, cementation and micritisation, is that initial mineralogies and textures can become quickly (syn-depositionally) overprinted, resulting in a secondary fabric that can be difficult to distinguish from a primary texture, though attempts have been made in the case of particular deposits such as speleothems (Frisia, 2015). For example, crystalline dendrite or banded crystalline fan dendritic cementstone fabrics (Della Porta, 2015) have been observed as primary precipitates (Gradzinski, 2010; Gandin and Capezzuoli, 2014; Brasier et al., 2015), but could also result from early diagenesis of 'boundstone' fabrics (sensu Della Porta, 2015), like micrite boundstone or micrite/microsparite boundstone and prismatic crystal fans with entombed microorganisms (Freytet and Verrecchia, 1999; Janssen et al., 1999; Arp et al., 2010; Gradzinski, 2010). It is therefore clear that sparry, equant or columnar calcitic crust fabrics do not unequivocally point to a diagenetic origin. Sparry or columnar calcite fabrics (Freytet et al., 1998; Janssen et al., 1999; Chafetz and Guidry, 2003; Brasier et al., 2011; 2015) and laminated, dense crusts of elongated calcite rays (Pentecost, 2005; Jones and Renaut, 2008; Jones and Peng, 2012b; Okumura et al., 2013) are reported, in the same depositional environments, as primary precipitates.

Is it however possible to provide some petrographic hints towards the recognition of precursors or primary, inherited textures in non-marine carbonates, affected - or not - by early diagenesis? Based on Freytet and Verrecchia (1999), Barton et al. (2001), Barton and Northup (2007), Gandin and Capezzuoli (2014), Brasier et al. (2015) and Frisia (2015):

- Fabric changes related to variations in depositional conditions such as temperature, flow rate (Fig. 9A, B).

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- Fabrics that are influenced by heterogeneities related to depositional processes: e.g. pellets, grains or micrite that stuck to the surface and interfered with crystal growth of overlying spar.
- Laminae that cap underlying crystals, with thickness variations depending on relative 'highs' and 'depressions' in the surface, and from which new crystals nucleate. (Fig. 9C, D)
- Abundance of fossilized microbial textures (filaments, rods, EPS, …) within certain laminae and their absence or change in habit, textures in over- and underlying laminae. Fabric changes are possibly co-eval with carbonate carbon isotopic changes.
- Entombed microbial filaments, not specifically located along crystal edges or cracks, and that affect the crystal habit or fabrics.
- Occurrence of particular crystal habits such as competitive crystal growth, undulose extinction in columnar calcite crystals, the presence of displacive cements and the absence of mechanical compaction.
- The preservation of primary unstable mineralogies, like aragonite and high-magnesium calcite.

None of these petrographic textures is, in isolation, sufficient to support an argument for the preservation of a primary fabric. Various lines of evidence, from for example petrographical, geochemical and microbiological analyses, must ideally be combined (Barton et al., 2001).

4.1.2 Impact of early diagenesis on microfabrics

So far, several valuable insights on the early diagenetic pathways of primary fabrics and microstructures have been obtained at sites where precipitation is ongoing and where fossil deposits are equally accessible (Freytet and Verrecchia, 1999; Janssen et al., 1999; Gandin and Capezzuoli, 2014; Brasier et al., 2015). The impact of early diagenesis on the primary fabric may vary in function of (i) a stable versus metastable primary mineralogy, (ii) crystal or grain size, (iii) rock/water ratio and

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water composition (Choquette and Pray, 1970; Lohmann, 1988; Morse and Mackenzie, 1990), and (iv) the dominant type of early diagenetic process. Precipitates consisting of a stable mineralogy at depositional conditions, like low-magnesium calcite, increase the likelihood of preserving initial textures and environmental geochemical signatures. Furthermore, it has been suggested that neomorphism of high-magnesium calcite to low-magnesium calcite occurs with little change in fabric as it does not entail a crystallographic change (James and Choquette, 1984; James and Jones, 2015), compared to more drastic cases where the mineralogical change was from aragonite to low-magnesian calcite.

Micrite and microsparite are more prone to neomorphism and replacement given their higher solubility as a result of their higher surface area: volume ratio (Flügel, 2004). When the rock: water ratio is low, a continuous supply of dilute fluids facilitates complete dissolution prior to cementation, resulting in fabric loss (James and Choquette, 1984). In cases where environmental changes can cause rapid changes in ion concentrations, pCO_2 of the ground-, surface and/or cave water, a strong potential for diagenetic modification exists as saturation states of mineral phases may rapidly change (Moore and Wade, 2013; Domínguez-Villar et al., 2017). Further, cementation processes that result in encasing of a primary fabric may tend to better preserve the original fabrics, whereas neomorphism, micritisation and dissolution tend to partially or even completely obliterate the primary fabric.

The possible effects neomorphism may have on the disappearance or appearance of laminations and layering deserve further discussion. The primary versus (early) diagenetic nature of lamination in spring carbonates or speleothems has important implications for their use as time-reference for seasonal, annual, decadal interpretations of paleoclimatic signals and geochronology (Wassenburg et al., 2012; Scholz et al., 2014; Zhang et al., 2014; Frisia, 2015). Arp et al. (2001) observed that over time tufa crusts form homogeneous, continuous layers of radial palisade calcite with sweeping extinction, only enclosing small fluid or gas inclusions and microcrystalline intercalations. Janssen et

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al. (1999) in their summarizing diagram suggest that laminations may actually become enhanced. Though the exact process remains to be clearly addressed, they suggested that growth of sparry crystals between micrite-encrusted cyanobacterial filaments caused horizontal sparry bands to form. Freytet et al. (1998) suggested another possible secondary, lamination-creation phenomenon that could occur through the ‘redistribution of organic matter’ during sparry crust formation. Here, organic matter clusters form either clots or internal laminations within larger crystals, resulting in a secondary, ‘micro-laminated fabric’.

In summary, many of the early diagenetic processes are constructive and result in an overall coarsening of the microfabric, with exception of (spar)micritisation. It further seems that early diagenesis affecting complex and diverse primary microfabrics leads to homogenization of features. This was documented by Golubić et al. (2008) for the diagenesis of calcified mosses, algae and cyanobacteria in both recent and fossil spring deposits. Similarly, at Mammoth Hot Springs, fresh precipitates show a wide range of aragonitic textures going from streamers to shrub crystal aggregates and spherulites (Fouke et al., 2000), whereas the fossil record in the Y-10 core (Yellowstone National Park, USA) suggests that coarse, sparry equant to radial, elongated crystals are dominantly preserved (Chafetz and Guidry, 2003). Progressive convergence of microfabrics through early diagenesis, suggested by microscopic comparisons, is an intriguing hypothesis that needs further testing in the field and in the lab.

Furthermore, even when no visible arguments are found for diagenetic alteration (Wassenburg et al., 2012; Ritter et al., 2015), for example, when replacement calcite inherits both textural and chemical properties of the precursor, very localized, open-system behavior may still cause resetting of an initial geochemical signal (Bajo et al., 2016). In both cases, it is then only by a careful comparison of different geochemical proxies along the same transect that localized domains of post-depositional alteration can be localized (Bajo et al., 2016).

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4.2 Timing and rates of early diagenesis

4.2.1 Onset of diagenesis in 'niches'

It has been shown that diagenesis of non-marine sediments encompasses a diverse suite of processes that can start immediately after initiation of deposition. The products of these very first transformation processes depend much on the diagenetic potential of initial metastable phases like ACC, vaterite, Ca-oxalates, huntite, hydromagnesite and aragonite (Freytet and Verrecchia, 1995; Sánchez-Román et al., 2011; Demény et al., 2016). Until now, these very first neomorphic and replacement processes have mostly been detected in studies on the mineralization of microbialites in (evaporative) lacustrine settings and in soils. It seems that for the processes so far visualized, organic matter and the micro-environments within EOM, but also at the micron-scale interface with Mg-silicates, play a crucial role in hosting these early transformations and control the location where precipitation and diagenesis starts (Freytet and Verrecchia, 1998; Peng and Jones, 2013; Burne et al., 2014; Pedley, 2014; Mercedes-Martín et al., 2016; Pace et al., 2016; Jones, 2017).

The recognition of very early stages of diagenesis and its associated fabrics and mineral products allows us to consider the templates on which these continually evolving rocks are built. It is necessary to learn how these systems really work in order to reverse-engineer them, and in doing so, unravel clues towards the initial and evolving physicochemical and (micro)biological conditions at deposition.

4.2.2 Rates ?

An evident question now is 'how fast is diagenesis?' and how to explain different rates at similar sites? Though the dataset is extremely limited (Table 2), the wide spread in assumed rates, from months to centuries, is apparent. In sites of active deposition, like carbonate formation in springs and streams, several studies have followed up on a single site over the course of several years. This gives some idea of diagenetic changes in the ranges of hours, days and months (Table 2). Furthermore,

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much radio-isotope dating work has focused on establishing reliable chronologies for climate proxies. Where diagenetic features are described and primary deposition could be dated, for example by ^{14}C from embedded wood or bone fragments (Rainey and Jones, 2007), rates for diagenetic processes could be roughly approximated. Frisia et al. (2002) present evidence that aragonite-to-calcite conversion in speleothems in the south of France can occur within 1000 years. Observations from springs at Mammoth Hot Springs (Yellowstone National Park, USA) show that calcite crystals replacing aragonite fibers happens in-situ, at the depositional surface while the spring is still active, and while microbial filaments of the Apron-Channel Facies are being encrusted with fine aragonite needles. This process must happen within days or weeks.

Strong contrasts have been reported in the preservation state of primary fabrics in similar continental carbonate deposits. Zamarreño et al. (1997) reported well-preserved oncoids, domes, laminated crusts and irregular bioherms in a Tertiary stream carbonate system (Ebro Basin, Spain). A similar depositional environment in Belgium however was said to reveal evidence for neomorphism, cementation and bio-erosion in Holocene deposits (Janssen et al., 1999). What, then, controls differences in rates of early diagenesis in similar settings (e.g. between the Belgian and Spanish stream carbonates)?

A first controlling parameter is the stability of the primary fabric mineral under depositional conditions. The more stable phases like low-magnesian calcite reduce the likelihood of pervasive early diagenetic recrystallization, thereby enhancing the chance for the preservation of geochemical proxies and the geochronology signal (Fairchild et al., 2006; Armenteros, 2010; Scholz et al., 2014). Aragonite–to–calcite inversion can be slowed down if there is no liquid phase to allow dissolution and re-precipitation (Bischoff and Fyfe, 1968) and it is inhibited by the presence of Mg^{2+} in solution (Kunzler and Goodell, 1970; Frisia et al., 2002). In aqueous solution, the aragonite–to–calcite transformation may be more rapid and spontaneous (24 h at 50° and 70 °C) (Berner, 1980; Zhou and Zheng, 2001). In phreatic, meteoric diagenetic environments, the time needed for

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aragonite–to–calcite conversion was calculated as 5–16 ka (Budd, 1988), and 10^5-10^6 years for the vadose freshwater zone (Morse and Mackenzie, 1990).

A second parameter, linked to the availability of a liquid phase, is the permeability of the primary deposits. With the exception of some dense, hot spring, crystalline crusts, calcretes and calcitic speleothems, most non-marine carbonate fabrics form rather open primary fabrics, with a variety of intergranular, intercrystalline, framework and structural cavities of variable size and shape (Ronchi and Cruciani, 2015; Soete et al., 2015). The high primary porosity allows the infiltration of waters that, at the surface, may still be involved in precipitation, but could change composition and initiate early diagenesis below (Frisia et al., 2002; Chafetz and Guidry, 2003). But also, very local scale, discontinuities (Bajo et al., 2016; Domínguez-Villar et al., 2017) and secondary porosity, like fractures, brecciation or desiccation cracks, can play an important role and provide efficient channels for infiltration, percolation, ascending fluids and lateral fluid circulation (Deitchman and Loheide, 2009; Frisia and Borsato, 2010; Gandin and Capezzuoli, 2014; Inverarity et al., 2016).

Furthermore, small -scale variations in porosity, permeability and water retained in pore space will cause diagenesis to proceed unevenly. As a result, within the same structure, like for example a tufa build-up, microscopic textures may become dissolved and re-arranged in one place whereas in another the texture remains more or less unchanged (Golubić et al., 2008; Martín-García et al., 2009; Melim and Spilde, 2011; Bajo et al., 2016). In contrast, where clay minerals (e.g. palygorskite) co-occur with primary precipitates, like in some palustrine or lacustrine deposits, they might be effective permeability barriers, retaining initial water compositions within the primary pores, and early diagenesis can be drastically slowed down (Arribas et al., 2004).

A third and critical controlling factor is climate, which may differ strongly for different geographical regions. The latter determines temperature, organic matter oxidation and the availability and composition of water, thereby affecting the degree of over- and under-saturation with respect to

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different mineral phases (Moore and Wade, 2013). Two extremes are warm tropical humid or cool arid and dry regions, the former leading to pronounced diagenesis, for example, in soil profiles.

4.3 A framework for understanding non-marine carbonate diagenesis?

From the range of diagenetic processes, fabrics and fluids involved, the need for an update and add-on to the classical diagenesis frameworks that chiefly focus on late stage major dissolution and minor cementation from meteoric waters within a ‘vadose’ and ‘phreatic’ context (James and Choquette, 1984; Lohmann, 1988; Morse and Mackenzie, 1990; Moore, 2001), is apparent. Here we focus on the so far poorly addressed early diagenesis in the non-marine environment, but the process-centered framework and approach may be equally extended towards later stages of diagenesis or could be applied to diagenesis in marine environments (Fig. 10).

One must start from the realization that non-marine depositional environments form a continuum in time and space, from spring to stream to soil to cave, and so are there rock products, and their diagenetic processes and drivers, their fabrics and fluids (Alonso-Zarza, 2003; Brasier et al., 2015; Della Porta, 2015). Each corner of the triangle in Figure 10 represents a group of processes, i.e. dissolution, cementation, and mechanical weathering that may act or dominate in each of these depositional environments. Replacement and neomorphism processes are placed between cementation and dissolution. Several of the early diagenetic microscopic to macroscopic fabrics and textures discussed earlier, are illustrated around the front triangle. The length axis of the prism shape represents time. Associated with progressing time may be processes related to increases in temperature and pressure due to sediment burial.

The evolving (paleo)environmental context is given by the arrows around the pyramid shape and include climate, dominant fluids, and the presence and degradation of organic matter (Baumgartner et al., 2006; Dupraz et al., 2009; Zhu and Dittrich, 2016). Armenteros (2010) suggested a similar early

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diagenesis domain and called it ‘eogenetic meteoric diagenesis’, in parallel with its denomination in the marine world. However, processes like weathering and pedogenesis were not included and were placed in a separate domain.

However, several gaps remain in our understanding of how primary, non-marine sediments and precipitates are exactly transformed into rocks found in the geological record and how this could (or not) affect the paleoclimatic archives preserved in these deposits. Syn- and post-depositional early diagenesis play a crucial role in this transformation. Focused case studies, where observations and monitoring of active carbonate deposition can be integrated with exposed or subsurface fossil deposits, could prove very insightful. In addition, an experimental approach, using in-vitro (Pedley, 2014; Mercedes-Martín et al., 2016) and in-situ (Melim and Spilde, 2011; Boch et al., 2015) setups could help investigate the exact processes, and diagenetic pathways (Ritter et al., 2017), controls and rates of individual transformations across the continuum of non-marine carbonate depositional contexts. A better understanding of short-lived intermediate steps and diagenetic products, and the effects on individual geochemical proxies (Wassenburg et al., 2012; Ritter et al., 2015) is needed to bridge a growing gap between current field and lab-based studies at the nanoscale, mostly focussed on the very first steps of carbonate nucleation and precipitation (Benzerara et al., 2006; Sánchez-Román et al., 2011; Krause et al., 2012; Roberts et al., 2013; Burne et al., 2014; Brauchli et al., 2016; Pace et al., 2016), and the fossil rock record of diagenetically modified deposits.

5. Final thoughts

(Early) diagenesis in non-marine carbonates is a broad topic, touching several other domains and research questions that were however not dealt with in detail here. From a geochemical point of view, only stable carbon-oxygen and clumped Δ_{47} isotopes were focused upon as they are still part of the most commonly used isotopes in carbonate research (Swart, 2015). Fluid inclusion studies

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however have a long history of applications in non-marine carbonates, in particular speleothems (Fairchild et al., 2006). Recently also advances have been made in the use of non-traditional isotopes such as Mg-isotopes (Buhl et al., 2007; Immenhauser et al., 2010; Riechelmann et al., 2012) and Ca-isotopes (Owen et al., 2016; Yan et al., 2016) to address paleoenvironmental and –climatic changes.

In parallel with the challenge to define and recognize primary fabrics, the search for criteria to distinguish sedimentary precipitates that result solely from physicochemical processes and those that formed in relation to biota (biogenecity) is raised (Freytet and Verrecchia, 1998; Sugitani et al., 2007; Oehler et al., 2009; Wacey, 2009; Jones, 2010; Knoll et al., 2013; Mettraux et al., 2015; Nutman et al., 2016). Early diagenesis may strongly complicate the determination of the biogenecity of a fabric (Brasier et al., 2015). Probing for organic geochemical signals using high-resolution- or cryo-TEM, STXM, Nano-SIMS and including trace elements, REE and molecular fossils like lipids and proteins, could shed light on the intimate association of organic molecules and mineral matrix (Benzerara et al., 2006; Blyth and Frisia, 2008; Wacey et al., 2010) to learn who was there and how they affected precipitation or alteration of carbonate phases.

Finally, it has also become apparent that with a better understanding of the pathways of early diagenesis fabric changes, the implications towards porosity-permeability evolution of non-marine carbonates could be better estimated, predicted and quantified (Fig. 11A, B Della Porta, 2015; Ronchi and Cruciani, 2015; Soete et al., 2015; De Boever et al., 2016; Claes et al., 2017a). Constructive processes, like cementation, syntaxial overgrowth and aggrading neomorphism often seem to dominate earliest stages of non-marine diagenesis. They may result in fabric stabilization, thereby potentially reducing compaction effects, but also in a tighter fabric of isolated micro- to macropores (De Boever et al., 2016). Soete et al. (2015) report on P-wave velocity versus porosity relations for ancient travertines that differ from those previously defined for marine carbonates. They found that acoustic velocity variations are linked to the dominant pore types present, but also that cementation causes a positive offset from the best-fit curve of acoustic velocity in function of porosity. Several

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aspects however still need further study, including the origin of micron-sized porosity in several of the microbial-related non-marine carbonates (Bosak et al., 2004; De Boever et al., 2016) and how to upscale the complex pore networks in for example shrub-containing lithologies (Claes et al., 2017b).

6. Conclusions

From this review of older and recent, ongoing work on non-marine carbonates and in particular the early diagenetic modifications they undergo, a few key messages can be retained:

- Diagenesis starts immediately after the first crystals have formed. The onset of diagenesis often takes places in niches or ‘micro-scale environments’, in relation to metastable phases, like ACC, vaterite, Ca-oxalates, hydrous Mg-carbonates and aragonite. Improved visualization techniques of fabric and mineralogical changes at very short time and spatial scales slowly result in a better understanding of processes and intermediary products.
- The presence and activity of microorganisms and organic matter seems to have a profound impact, not only on the precipitation of carbonates, but also the micron-scale localization of different early diagenetic replacement processes that rapidly transform the primary microfabrics, in places – and probably more widespread than currently documented – in tight association with authigenic clays like Mg-silicates.
- Early diagenesis seems to be mostly a constructive (and not destructive) process. It often results in a coarsening of the fabrics and even seems to homogenize initially very different microfabrics, though this is a hypothesis that should be further checked.
- Timing in continental diagenesis is one of the most challenging parameters to assess. Given the early start and sometimes observed fast rates (minutes to hours and days), non-marine carbonates found in the rock record have likely been subject to fabric and possibly mineralogical and geochemical changes.

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- The very early diagenetic impact of diagenesis on traditional and less conventional isotope geochemical proxies used in long-term paleoclimatic and paleoenvironmental studies may potentially be insignificant, but is not sufficiently well understood to say this with certainty. Especially a combination of trace element, isotope and dating compiled in transects proves useful in the detection of pristine zones and selective diagenetic alteration even when no petrographically visible traces of diagenesis are found. Increasingly higher resolution geochemical analysis for geochronology and paleoclimatic records should also go hand in hand with an improved understanding of initial precipitation and early diagenetic processes. Where (micro-)organisms or the assembly of amorphous precursors play a role in crystal formation, fractionation or inherited signals could obliterate an environmental representative signal.
- There is a need for more field and lab-based experimental approaches to reveal steps in early diagenetic processes from the fabric and as well as from the geochemical proxy point of view. This will contribute to bridging the gap between our understanding of early, precipitation and modification processes at the nanoscale and the micro- and macrofabrics preserved in the geological record.
- Instead of a realm based view on diagenesis, a process-centered framework is proposed to address (early) diagenesis in the non-marine carbonates. This may constitute an add-on to existing schemes and diagenetic frameworks that allows to better address and depict the diversity of processes happening in the early stages of non-marine diagenesis.

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ACCEPTED MANUSCRIPT

References

Affek, H.P., Bar-Matthews, M., Ayalon, A., Matthews, A., Eiler, J.M., 2008. Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by “clumped isotope” thermometry. Geochimica et Cosmochimica Acta 72, 5351–5360. doi:10.1016/j.gca.2008.06.031

Affek, H.P., Zaarur, S., 2014. Kinetic isotope effect in CO_2 degassing: Insight from clumped and oxygen isotopes in laboratory precipitation experiments. Geochimica et Cosmochimica Acta 143, 319–330. doi:10.1016/j.gca.2014.08.005

Allan, J.R., Matthews, R.K., 1982. Isotope signatures associated with early meteoric diagenesis.

ACCEPTED MANUSCRIPT

Sedimentology 29, 797–817.

Alonso-Zarza, A.M., 2003. Palaeoenvironmental significance of palustrine carbonates and calcretes in the geological record. Earth-Science Reviews 60, 261–298. doi:10.1016/S0012-8252(02)00106-X

Alonso-Zarza, A.M., Martín-Pérez, A., 2008. Dolomite in caves: Recent dolomite formation in oxic, non-sulfate environments. Castañar Cave, Spain. Sedimentary Geology 205, 160–164. doi:10.1016/j.sedgeo.2008.02.006

Alonso-Zarza, A.M., Tanner, L.H. (Eds.), 2010a. Carbonates in continental settings - Facies, Environments and Processes, Developments in Sedimentology 61. Elsevier, Amsterdam. doi:10.1016/S0070-4571(09)06106-8

Alonso-Zarza, A.M., Tanner, L.H. (Eds.), 2010b. Carbonates in continental settings - Geochemistry, Diagenesis and Applications, Developments in Sedimentology 62. Elsevier, Amsterdam. doi:10.1016/S0070-4571(09)06106-8

Andrews, J.E., 2006. Palaeoclimatic records from stable isotopes in riverine tufas: Synthesis and review. Earth-Science Reviews 75, 85–104. doi:10.1016/j.earscirev.2005.08.002

Andrews, J.E., Coletta, P., Pentecost, A., Riding, R., Dennis, S., Dennis, P.F., Spiro, B., 2004. Equilibrium and disequilibrium stable isotope effects in modern charophyte calcites: Implications for palaeoenvironmental studies. Palaeogeography, Palaeoclimatology, Palaeoecology 204, 101–114. doi:10.1016/S0031-0182(03)00725-9

Andrews, J.E., Riding, R., 2000. Depositional facies and aqueous-solid geochemistry of travertine-depositing hot springs (Angel Terrace, Mammoth Hot springs, Yellowstone National Park, U.S.A.) - Discussion. Journal of Sedimentary Research 71, 496–497.

Armenteros, I., 2010. Diagenesis of Carbonates in Continental Settings. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds.), Carbonates in Continental Settings: Geochemistry, Diagenesis and

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Applications. Developments in Sedimentology 62. Elsevier, Amsterdam, pp. 61–151.

Armenteros, I., Bustillo, M.A., Blanco, L.A., 1995. Pedogenic and groundwater processes in a closed Miocene basin (northern Spain). Sedimentary Geology 99, 17–36.

Arp, G., 1995. Lacustrine bioherms, spring mounds, and marginal carbonates of the Ries-impact-crater (Miocene, Southern Germany). Facies 33, 35–89. doi:10.1007/BF02537444

Arp, G., Bissett, A., Brinkmann, N., Cousin, S., Beer, D. de, Friedl, T., Mohr, K.I., Neu, T.R., Reimer, A., Shiraishi, F., Stackebrandt, E., Zippel, B., 2010. Tufa-forming biofilms of German karstwater streams: microorganisms, exopolymers, hydrochemistry and calcification. In: Pedley, H.M., Rogerson, M. (Eds.), Tufas and Speleothems: Unravelling the Microbial and Physical Controls. Geological Society, London, pp. 83–118.

Arp, G., Blumenberg, M., Hansen, B.T., Jung, D., Kolepka, C., Lenz, O., Nolte, N., Poschlod, K., Reimer, A., Thiel, V., 2013a. Chemical and ecological evolution of the Miocene Ries impact crater lake, Germany: A reinterpretation based on the Enkingen (SUBO 18) drill core. Bulletin of the Geological Society of America 125, 1125–1145. doi:10.1130/B30731.1

Arp, G., Hansen, B.T., Pack, A., Reimer, A., Schmidt, B.C., Simon, K., Jung, D., 2017. The soda lake—mesosaline halite lake transition in the Ries impact crater basin (drilling Löpsingen 2012, Miocene, southern Germany). Facies 63, 1. doi:10.1007/s10347-016-0483-7

Arp, G., Hofmann, J., Reitner, J., 1998. Microbial Fabric Formation in Spring Mounds (“Microbialites”) of Alkaline Salt Lakes in the Badain Jaran Sand Sea, PR China. Palaios 13, 581–592.

Arp, G., Kolepka, C., Simon, K., Karius, V., Nolte, N., Hansen, B.T., 2013b. New evidence for persistent impact-generated hydrothermal activity in the Miocene Ries impact structure, Germany. Meteoritics and Planetary Science 48, 2491–2516. doi:10.1111/maps.12235

Arp, G., Reimer, A., Reitner, J., 2003. Microbialite Formation in Seawater of Increased Alkalinity,

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Satonda Crater Lake, Indonesia. Journal of Sedimentary Research 73, 105–127. doi:10.1306/071002730105

Arp, G., Wedemeyer, N., Reitner, J., 2001. Fluvial tufa formation in a hard-water creek (Deinschwanger Bach, Franconian Alb, Germany). Facies 44, 1–22. doi:10.1007/BF02668163

Arribas, M.E., Bustillo, M.A., Tsige, M., 2004. Lacustrine chalky carbonates: Origin, physical properties and diagenesis (Palaeogene of the Madrid Basin, Spain). Sedimentary Geology 166, 335–351. doi:10.1016/j.sedgeo.2004.01.012

Awramik, S.M., Buchheim, H.P., 2009. A giant, Late Archean lake system: The Meentheena Member (Tumbiana Formation; Fortescue Group), Western Australia. Precambrian Research 174, 215–240. doi:10.1016/j.precamres.2009.07.005

Bajo, P., Hellstrom, J., Frisia, S., Drysdale, R., Black, J., Woodhead, J., Borsato, A., Zanchetta, G., Wallace, M.W., Regattieri, E., Haese, R., 2016. “Cryptic” diagenesis and its implications for speleothem geochronologies. Quaternary Science Reviews 148, 17–28. doi:10.1016/j.quascirev.2016.06.020

Barazzuoli, P., Costantini, A., Fondi, R., Gandin, A., Ghezzo, C., Lazzarotto, A., Micheluccini, M., Salleolini, M., Salvadori, L., 1988. A geological and geological technical profile of Rapolano travertines. In: Coli, V. (Ed.), Travertine from Siena. Al.Sa.Ba Grafiche, Siena, pp. 26–35.

Barth, J.A., Chafetz, H.S., 2015. Cool water geyser travertine: Crystal Geyser, Utah, USA. Sedimentology 62, 607–620. doi:10.1111/sed.12158

Barton, H.A., Northup, D.E., 2007. Geomicrobiology in cave environments: Past, current and future perspectives. Journal of Cave and Karst Studies 69, 163–178.

Barton, H.A., Spear, J.R., Pace, N.R., 2001. Microbial Life in the Underworld: Biogenicity in Secondary Mineral Formations. Geomicrobiology Journal 18, 359–368. doi:10.1080/01490450152467840

ACCEPTED MANUSCRIPT

Bary, A. de, 1887. Comparative Morphology and Biology of the Fungi, Mycetozoa and Bacteria. Clarendon Press, Oxford, UK.

Bathurst, R.G.C., 1975. Carbonate sediments and their diagenesis, 2nd ed. Elsevier Science B.V., Amsterdam, the Netherlands. doi:10.1016/0016-7185(73)90072-9

Baumgartner, L.K., Reid, R.P., Dupraz, C., Decho, a. W., Buckley, D.H., Spear, J.R., Przekop, K.M., Visscher, P.T., 2006. Sulfate reducing bacteria in microbial mats: Changing paradigms, new discoveries. Sedimentary Geology 185, 131–145. doi:10.1016/j.sedgeo.2005.12.008

Benzerara, K., Meibom, a., Gautier, Q., Kazmierczak, J., Stolarski, J., Menguy, N., Brown, G.E., 2010. Nanotextures of aragonite in stromatolites from the quasi-marine Satonda crater lake, Indonesia. Geological Society, London, Special Publications 336, 211–224. doi:10.1144/SP336.10

Benzerara, K., Menguy, N., López-García, P., Yoon, T.-H., Kazmierczak, J., Tyliszczak, T., Guyot, F., Brown, G.E., 2006. Nanoscale detection of organic signatures in carbonate microbialites. Proceedings of the National Academy of Sciences of the United States of America 103, 9440–9445. doi:10.1073/pnas.0603255103

Benzerara, K., Skouri-Panet, F., Li, J., Ferard, C., Gugger, M., Laurent, T., Couradeau, E., Ragon, M., Cosmidis, J., Menguy, N., Margaret-Oliver, I., Tavera, R., Lopez-Garcia, P., Moreira, D., 2014. Intracellular Ca-carbonate biomineralization is widespread in cyanobacteria. Proceedings of the National Academy of Sciences 1–6. doi:10.1073/pnas.1403510111

Bergman, S.C., Huntington, K.W., Crider, J.G., 2013. Tracing paleofluid sources using clumped isotope thermometry of diagenetic cements along the Moab Fault, Utah. American Journal of Science 313, 490–515. doi:10.2475/05.2013.03

Berner, R.A., 1980. Early Diagenesis: A Theoretical Approach. Princeton Series in Geochemistry.

ACCEPTED MANUSCRIPT

Princeton University Press, Princeton, New Jersey, USA.

Bindschedler, S., Millière, L., Cailleau, G., Job, D., Verrecchia, E.P., 2010. Calcitic nanofibres in soils and caves: a putative fungal contribution to carbonatogenesis. In: Pedley, H.M., Rogerson, M.R. (Eds.), Tufas and Speleothems: Unravelling the Microbial and Physical Controls. Geological Society, London, pp. 225–238.

Bischoff, J.L., Fyfe, W.S., 1968. Catalysis, inhibition and the calcite-aragonite problem. I. The aragonite-calcite transformation. American Journal of Science 266, 80–90.

Bischoff, J.L., Stine, S., Rosenbauer, R.J. Fitzpatrick, J.A., Stafford Jr., T.W., Herbst, D.B., Rosenbauer, R.J., 1993. Ikaite precipitation by mixing of shoreline springs and lake water, Mono Lake, California, USA. Geochmica et Cosmochimica Acta 57, 3855–3865.

Bissett, A., Reimer, A., Beer, D. De, Shiraishi, F., Arp, G., 2008. Metabolic microenvironmental control by photosynthetic biofilms under changing macroenvironmental temperature and pH conditions. Applied and Environmental Microbiology 74, 6306–6312. doi:10.1128/AEM.00877-08

Blyth, A.J., Frisia, S., 2008. Molecular Evidence for Bacterial Mediation of Calcite Formation in Cold High-Altitude Caves. Geomicrobiology Journal 25, 101–111. doi:10.1080/01490450801934938

Boch, R., Dietzel, M., Reichl, P., Leis, A., Baldermann, A., Mittermayr, F., Pölt, P., 2015. Rapid ikaite ($CaCO_3 \cdot 6H_2O$) crystallization in a man-made river bed: Hydrogeochemical monitoring of a rarely documented mineral formation. Applied Geochemistry 63, 366–379. doi:10.1016/j.apgeochem.2015.10.003

Boever, E. De, Foubert, A., Lopez, B., Swennen, R., Jaworowski, C., Özkul, M., Virgone, A., 2017. Comparative study of the Pleistocene Cakmak Quarry (Denizli Basin, Turkey) and Modern Mammoth Hot Springs deposits (Yellowstone National Park, USA): Towards an integrated

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Travertine Depositional Facies Model? Quaternary International 437, 129–146.

Boever, E. De, Foubert, A., Oligschlaeger, D., Claes, S., Soete, J., Bertier, P., Özkul, M., Virgone, A., Swennen, R., 2016. Quantification of porosity in continental spring carbonate facies - Case study from plugs of the Cakmak quarry (Denizli, Turkey). Geochem. Geophys. Geosyst. 17, 2922–2939.

Böhm, F., Joachimski, M.M., Dullo, W.-C., Eisenhauer, A., Lehnert, H., Reitner, J., Wörheide, G., 2000. Oxygen isotope fractionation in marine aragonite of coralline sponges. Geochmica et Cosmochimica Acta 64, 1695–1703.

Bolhar, R., Kranendonk, M.J. Van, 2007. A non-marine depositional setting for the northern Fortescue Group, Pilbara Craton, inferred from trace element geochemistry of stromatolitic carbonates. Precambrian Research 155, 229–250. doi:10.1016/j.precamres.2007.02.002

Bontognali, T.R.R., Mckenzie, J.A., Warthmann, R.J., Vasconcelos, C., 2014. Microbially influenced formation of Mg-calcite and Ca-dolomite in the presence of exopolymeric substances produced by sulphate-reducing bacteria. Terra Nova 26, 72–77. doi:10.1111/ter.12072

Bontognali, T.R.R., Vasconcelos, C., Warthmann, R.J., Bernasconi, S.M., Dupraz, C., Strohmenger, C.J., Mckenzie, J.A., 2010. Dolomite formation within microbial mats in the coastal sabkha of Abu Dhabi (United Arab Emirates). Sedimentology 57, 824–844. doi:10.1111/j.1365-3091.2009.01121.x

Bosak, T., Souza-Egipsy, V., Corsetti, F. a., Newman, D.K., 2004. Micrometer-scale porosity as a biosignature in carbonate crusts. Geology 32, 781–784. doi:10.1130/G20681.1

Bots, P., Benning, L.G., Rodriguez-Blanco, J.-D., Roncal-Herrero, T., Shaw, S., 2012. Mechanistic insights into the crystallization of amorphous calcium carbonate (ACC). Crystal Growth and Design 12, 3806–3814. doi:10.1021/cg300676b

Bouton, A., Vennin, E., Boulle, J., Pace, A., Bourillot, R., Thomazo, C., Brayard, A., Désaubliaux, G., Goslar, T., Yokoyama, Y., Dupraz, C., Visscher, P.T., 2016a. Linking the distribution of microbial deposits from the Great Salt Lake (Utah, USA) to tectonic and climatic processes. Biogeosciences 13, 5511–5526. doi:10.5194/bg-13-5511-2016

Bouton, A., Vennin, E., Mulder, T., Pace, A., Bourillot, R., Thomazo, C., Brayard, A., Goslar, T., Buoncristiani, J.F., Désaubliaux, G., Visscher, P.T., 2016b. Enhanced development of lacustrine microbialites on gravity flow deposits, Great Salt Lake, Utah, USA. Sedimentary Geology 341, 1–12. doi:10.1016/j.sedgeo.2016.05.004

Braissant, O., Cailleau, G., Aragno, M., Verrecchia, E.P., 2004. Biologically induced mineralization in the Iroko Milicia excelsa (Moraceae): its causes and consequences to the environment. Geobiology 2, 59–66.

Braissant, O., Verrecchia, E.P., Aragno, M., 2002. Is the contribution of bacteria to terrestrial carbon budget greatly underestimated? Naturwissenschaften 89, 366 – 370.

Brasier, A.T., 2011. Searching for travertines, calcretes and speleothems in deep time: Processes, appearances, predictions and the impact of plants. Earth-Science Reviews 104, 213–239. doi:10.1016/j.earscirev.2010.10.007

Brasier, A.T., Rogerson, M.R., Mercedes-Martín, R., Vonhof, H.B., Reijmer, J.J.G., 2015. A Test of the Biogenicity Criteria Established for Microfossils and Stromatolites on Quaternary Tufa and Speleothem Materials Formed in the “Twilight Zone” at Caerwys, UK. Astrobiology 15, 883–900. doi:10.1089/ast.2015.1293

Brauchli, M., McKenzie, J.A., Strohmenger, C.J., Sadooni, F., Vasconcelos, C., Bontognali, T.R.R., 2016. The importance of microbial mats for dolomite formation in the Dohat Faishakh sabkha, Qatar. Carbonates and Evaporites 31, 339–345. doi:10.1007/s13146-015-0275-0

Brinkmann, N., Hodač, L., Mohr, K.I., Hodačová, A., Jahn, R., Ramm, J., Hallmann, C., Arp, G., Friedl, T.,

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

2015. Cyanobacteria and Diatoms in Biofilms of Two Karstic Streams in Germany and Changes of Their Communities Along Calcite Saturation Gradients. Geomicrobiology Journal 32, 255–274. doi:10.1080/01490451.2014.901438

Brogi, A., Capezzuoli, E., 2008. Travertine deposition and faulting: the fault-related travertine fissure-ridge at Terme S. Giovanni, Rapolano Terme (Italy). International Journal of Earth Sciences 98, 931–947. doi:10.1007/s00531-007-0290-z

Brogi, A., Capezzuoli, E., Gandin, A., Siena, U., Laterina, V., Brogi, R.A., Capezzuoli, E., Gandin, A., Rapolano, S.G., Settentrionale, A., 2007. I Travertini delle Terme di S. Giovanni (Rapolano Terme, Appennino Settentrionale) e loro Implicazione Neotettonica 20, 107–124.

Budd, D.A., 1988. Aragonite-to-calcite transformation during fresh-water diagenesis of carbonates: Insights from pore-water chemistry. GSA Bulletin 100, 1260–1270.

Buhl, D., Immenhauser, A., Smeulders, G., Kabiri, L., Richter, D.K., 2007. Time series δ^{26}Mg analysis in speleothem calcite: Kinetic versus equilibrium fractionation, comparison with other proxies and implications for palaeoclimate research. Chemical Geology 244, 715–729. doi:10.1016/j.chemgeo.2007.07.019

Burne, R. V., Moore, L.S., Christy, A.G., Troitzsch, U., King, P.L., Carnerup, A.M., Joseph Hamilton, P., 2014. Stevensite in the modern thrombolites of Lake Clifton, Western Australia: A missing link in microbialite mineralization? Geology 42, 575–578. doi:10.1130/G35484.1

Bustillo, M.A., 2010. Silicification of Continental Carbonates. In: Alonso-Zarza, A.M., Tanner, T.C. (Eds.), Carbonates in Continental Settings: Geochemistry, Diagenesis and Applications. Developments in Sedimentology 62. Elsevier B.V., Amsterdam, pp. 153–178.

Bustillo, M.A., Alonso-Zarza, A.M., 2007. Overlapping of pedogenesis and meteoric diagenesis in distal alluvial and shallow lacustrine deposits in the Madrid Miocene Basin, Spain. Sedimentary

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Geology 198, 255–271. doi:10.1016/j.sedgeo.2006.12.006

Bustillo, M.A., Arribas, M.E., Bustillo, M., 2002. Dolomitization and silicification in low-energy lacustrine carbonates (Paleogene, Madrid Basin, Spain). Sedimentary Geology 151, 107–126. doi:10.1016/S0037-0738(01)00234-2

Cailleau, G., Braissant, O., Verrecchia, E., 2011. Turning sunlight into stone: the oxalate–carbonate pathway in a tropical tree ecosystem. Biogeosciences 8, 1755–1767.

Cailleau, G., Braissant, O., Verrecchia, E.P., 2004. Biomineralization in plants as a long-term carbon sink. Naturwissenschaften 91, 191–194. doi:10.1007/s00114-004-0512-1

Cailleau, G., Mota, M., Bindschedler, S., Junier, P., Verrecchia, E.P., 2014. Detection of active oxalate-carbonate pathway ecosystems in the Amazon Basin: Global implications of a natural potential C sink. Catena 116, 132–141. doi:10.1016/j.catena.2013.12.017

Cailleau, G., Verrecchia, E.P., Braissant, O., Emmanuel, L., 2009. The biogenic origin of needle fibre calcite. Sedimentology 56, 1858–1875. doi:10.1111/j.1365-3091.2009.01060.x

Calvo, J.P., Blanc-Valleron, M.M., Rodríguez-Aranda, J.P., Rouchy, J.M., Sanz, M.E., 1999. Authigenic clay minerals in continental evaporitic environments. Spec. Publ. Int. Ass. Sedimentology 27, 129–151.

Calvo, J.P., Jones, B.F., Bustillo, M.A., Fort, R., Alonso, A.M., Kendall, C., 1995. Sedimentology and geochemistry of carbonates from lacustrine sequences in the Madrid Basin, Central Spain. Chemical Geology 123, 173–191.

Capezzuoli, E., Gandin, A., Pedley, M., 2014. Decoding tufa and travertine (fresh water carbonates) in the sedimentary record: The state of the art. Sedimentology 61, 1–21. doi:10.1111/sed.12075

Chafetz, H.S., Guidry, S.A., 2003. Deposition and diagenesis of Mammoth Hot Springs travertine, Yellowstone National Park, Wyoming, USA. Canadian Journal of Earth Sciences 40, 1515–1529.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

doi:10.1139/E03-051

Chafetz, H.S., Srdoc, D., Horvatincic, N., 1994. Early Diagenesis of Plitvice Lakes Waterfall and Barrier Travertine Deposits. Géographie physique et Quaternaire 48, 247–255.

Chidsey, T.C., Berg, M.D. Vanden, Eby, D.E., 2015. Petrography and characterization of microbial carbonates and associated facies from modern Great Salt Lake and Uinta Basin's Eocene Green River Formation in Utah, USA. In: Bosence, D.W.J., Gibbons, K.A., Heron, D.P. Le, Morgan, W.A., Pritchard, T., Vining, B.A. (Eds.), Microbial Carbonates in Space and Time: Implications for Global Exploration and Porduction. Special Publication 418. Geological Society of London, London, pp. 261–286.

Choquette, P.W., Pray, L.C., 1970. Geological nomenclature and classification of porosity in sedimentary carbonates. AAPG Bulletin 54, 207–250.

Cipriani, N., Malesani, P., Vannucci, S., 1977. I travertini dell'Italia centrale. Boll. Serv. Geol. Ital. 98, 85–115.

Claes, H., Erthal, M.M., Soete, J., Özkul, M., Swennen, R., 2017a. Petrography of travertine shrubs from the Ballık-Belevi area (Denizli, SW Turkey) as a potential analogue for Pre-Salt reservoir "microbialites": Shrub and pore type classification. AAPG Bulletin 1–17. doi:http://dx.doi.org/10.1016/j.quaint.2016.11.002

Claes, H., Marques-Erthal, M., Soete, J., Özkul, M., Swennen, R., 2017b. Shrub and pore type classification: Petrography of travertine shrubs from the Ballık-Belevi area (Denizli, SW Turkey). Quaternary International 217, 147–163.

Claes, H., Soete, J., Noten, K. Van, Desouky, H., Erthal, M.M. El, Vanahecke, F. Özkul, M., Swennen, R., 2015. Sedimentology, 3D geobody reconstruction and CO_2-source delineation of travertine palaeo-deposits in the Ballık area. Sedimentology 62, 1408–1445. doi:10.1111/sed.12188

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Claes, S., Soete, J., Cnudde, V., Swennen, R., 2016. A three-dimensional classification for mathematical pore shape description in complex carbonate reservoir rocks. Mathematical Geosciences 48, 619–639. doi:10.1007/s11004-016-9636-z

Coplen, T.B., 2007. Calibration of the calcite-water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. Geochimica et Cosmochimica Acta 71, 3948–3957. doi:10.1016/j.gca.2007.05.028

Council, T.C., Bennett, P.C., 1993. Geochemistry of ikaite formation at Mono Lake, California: Implications for the origin of tufa mounds. Geology 21, 971–974. doi:10.1130/0091-7613(1993)021<0971

Couradeau, E., Benzerara, K., Gerard, E., Moreira, D., Bernard, S., Brown, G.E., Lopez-Garcia, P., 2012. An Early-Branching Microbialite Cyanobacterium Forms Intracellular Carbonates. Science 336, 459–462. doi:10.1126/science.1216171

Cromack, K., Sollins, J.P., Todd, R.L., Fogel, R., Todd, A.W., Fender, W.M., Crossley, M.E., Crossley, D.A.J., 1977. The role of oxalic acid and bicarbonate in calcium cycling by fungi and bacteria : some possible implications for soil animals. Ecological Bulletin, Stockholm 25, 246–252.

Currey, D.R., James, S.R., 1982. Paleoenvironments of the northeastern Great Basin and northeastern Basin rim region: a review of geological and biological evidence. In: Madsen, D.B., O’Connel, J.F. (Eds.), Man and Environment in the Great Basin. Soc. American Archaeology Papers, pp. 27–52.

Currey, D.R., Oviatt, C.G., 1985. Durations, average rates, and probable causes of Lake Bonneville expansions, stillstands, and contractions during the last deep-lake cycle, 32,000 to 10,000 years ago. In: Kay, P.A., Diaz, H.F. (Eds.), Problems of and Prospects for Predicting Great Salt Lake Levels. University of Utah Center for Public Affairs and Administration, Salt Lake City, pp. 9–24.

Daëron, M., Guo, W., Eiler, J., Genty, D., Blamart, D., Boch, R., Drysdale, R.N., Maire, R., Wainer, K.,

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Zanchetta, G., 2011. 13C–18O clumping in speleothems: observations from natural caves and precipitation experiments. Geochimica et Cosmochimica Acta 75, 3303–3317. doi:10.1016/j.gca.2010.10.032

Davaud, E., Girardclos, S., 2001. Recent Freshwater Ooids and Oncoids from Western Lake Geneva (Switzerland): Indications of a Common Organically Mediated Origin. Journal of Sedimentary Research 71, 423–429. doi:10.1306/2dc40950-0e47-11d7-8643000102c1865d

Decho, A.W., Visscher, P.T., Reid, R.P., 2005. Production and cycling of natural microbial exopolymers (EPS) within a marine stromatolite. Palaeogeography, Palaeoclimatology, Palaeoecology 219, 71–86. doi:10.1016/j.palaeo.2004.10.015

Deitchman, R.S., Loheide, S.P., 2009. Ground-based thermal imaging of groundwater flow processes at the seepage face. Geophysical Research Letters 36, 1–6. doi:10.1029/2009GL038103

Demény, A., Németh, P., Czuppon, G., Leél-Őssy, S., Szabó, M., Judik, K., Németh, T., Stieber, J., 2016. Formation of amorphous calcium carbonate in caves and its implications for speleothem research. Scientific Reports 6, 39602. doi:10.1038/srep39602

Demichelis, R., Raiteri, P., Gale, J.D., 2014. Structure of hydrated calcium carbonates: A first-principles study. Journal of Crystal Growth 401, 33–37. doi:10.1016/j.jcrysgro.2013.10.064

Dennis, K.J., Schrag, D.P., 2010. Clumped isotope thermometry of carbonatites as an indicator of diagenetic alteration. Geochimica et Cosmochimica Acta 74, 4110–4122.

Deocampo, D.M., 2010. The Geochemistry of Continental Carbonates. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds.), Carbonates in Continental Settings: Geochemistry, Diagenesis and Applications. Developments in Sedimentology 62. Elsevier, Amsterdam, pp. 1–60.

Dietzel, M., Tang, J., Leis, A., Köhler, S.J., 2009. Oxygen isotopic fractionation during inorganic calcite precipitation - Effects of temperature, precipitation rate and pH. Chemical Geology 268, 107–

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

115. doi:10.1016/j.chemgeo.2009.07.015

Domínguez-Villar, D., Krklec, K., Pelicon, P., Fairchild, I.J., Cheng, H., Edwards, L.R., 2017. Geochemistry of speleothems affected by aragonite to calcite recrystallization – Potential inheritance from the precursor mineral. Geochimica et Cosmochimica Acta 200, 310–329. doi:10.1016/j.gca.2016.11.040

Dongen, B.E. van, Roberts, A.P., Schouten, S., Jiang, W.-T., Florindo, F., Pancost, R.D., 2007. Formation of iron sulfide nodules during anaerobic oxidation of methane. Geochimica et Cosmochimica Acta 71, 5155–5167.

Driessche, A. van, Kellermeier, M., Benning, L.G., Gebauer, D. (Eds.), 2017. New Perspectives on Mineral Nucleation and Growth. From Solution Precursors to Solid Material. Springer International Publishing Switzerland.

Dupraz, C., Reid, R.P., Braissant, O., Decho, A.W., Norman, R.S., Visscher, P.T., 2009. Processes of carbonate precipitation in modern microbial mats. Earth-Science Reviews 96, 141–162. doi:10.1016/j.earscirev.2008.10.005

Dupraz, C., Visscher, P.T., 2005. Microbial lithification in marine stromatolites and hypersaline mats. Trends in Microbiology 13, 429–438. doi:10.1016/j.tim.2005.07.008

Dupraz, C., Visscher, P.T., Baumgartner, L.K., Reid, R.P., 2004. Microbe-mineral interactions: Early carbonate precipitation in a hypersaline lake (Eleuthera Island, Bahamas). Sedimentology 51, 745–765. doi:10.1111/j.1365-3091.2004.00649.x

Eardley, A.J., 1938. Sediments of Great Salt Lake, Utah. AAPG Bulletin 22, 1305–1411.

Eiler, J.M., 2011. Paleoclimate reconstruction using carbonate clumped isotope thermometry. Quaternary Science Reviews 30, 3575–3588. doi:10.1016/j.quascirev.2011.09.001

Eiler, J.M., 2007. “Clumped-isotope” geochemistry-The study of naturally-occurring, multiply-

ACCEPTED MANUSCRIPT

substituted isotopologues. Earth and Planetary Science Letters 262, 309–327. doi:10.1016/j.epsl.2007.08.020

Eren, M., 2007. Genesis of Tepees in the Quaternary Hardpan Calcretes, Mersin, S Turkey. Carbonates and 123–134.

Eugster, H.P., Jones, B.F., 1979. Behavior of major solutes during closed basin-lakes brine evolution. American Journal of Science. doi:10.2475/ajs.279.6.609

Fairchild, I.J., Baker, A., 2012. Speleothem science: from process to past environments. John Wiley and Sons, Oxford, UK.

Fairchild, I.J., Fleming, E.J., Bao, H., Benn, D.I., Boomer, I., Dublyansky, Y. V., Halverson, G.P., Hambrey, M.J., Hendy, C., McMillan, E.A., Spötl, C., Stevenson, C.T.E., Wynn, P.M., 2016. Continental carbonate facies of a Neoproterozoic panglaciation, north-east Svalbard. Sedimentology 63, 443–497. doi:10.1111/sed.12252

Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Mattey, D., McDermott, F., 2006. Modification and preservation of environmental signals in speleothems. Earth-Science Reviews 75, 105–153. doi:10.1016/j.earscirev.2005.08.003

Fairchild, I.J., Treble, P.C., 2009. Trace elements in speleothems as recorders of environmental change. Quaternary Science Reviews 28, 449–468. doi:10.1016/j.quascirev.2008.11.007

Falk, E.S., Guo, W., Paukert, A.N., Matter, J.M., Mervine, E.M., Kelemen, P.B., 2016. Controls on the stable isotope compositions of travertine from hyperalkaline springs in Oman: Insights from clumped isotope measurements. Geochimica et Cosmochimica Acta 192, 1–28. doi:10.1016/j.gca.2016.06.026

Ferry, J.M., Passey, B.H., Vasconcelos, C., Eiler, J.M., 2011. Formation of dolomite at 40–80 °C in the Latemar carbonate buildup, Dolomites, Italy, from clumped isotope thermometry. Geology 39,

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

571–574. doi:10.1130/G31845.1

Field, L.P., Milodowski, A.E., Shaw, R.P., Stevens, L.A., Hall, M.R., Kilpatrick, A., Gunn, J., Kemp, S.J., Ellis, M.A., 2017. Unusual morphologies and the occurrence of pseudomorphs after ikaite ($CaCO_3 \bullet 6H_2O$) in fast growing, hyperalkaline speleothems. Mineralogical Magazine 81, 565–589. doi:10.1180/minmag.2016.080.111

Filippis, L. De, Faccenna, C., Billi, a., Anzalone, E., Brilli, M., Ozkul, M., Soligo, M., Tuccimei, P., Villa, I.M., 2012. Growth of fissure ridge travertines from geothermal springs of Denizli Basin, western Turkey. Geological Society of America Bulletin 124, 1629–1645. doi:10.1130/B30606.1

Fisher, R.S., 1988. Clay Minerals in Evaporite Host Rocks, Palo Duro Basin, Texas Panhandle. Journal of Sedimentary Petrology 58, 836–844.

Flügel, E., 2004. Microfacies of Carbonate Rocks. Analysis, Interpretation and Application. Springer-Verlag, Berlin Heidelberg.

Folk, R.L., 1965. Petrology of Sedimentary Rocks. Hemphill Publishing Company, Austin, Texas 78703.

Folk, R.L., Assereto, R., 1976. Comparative fabrics of length-slow and length-fast calcite and calcitized aragonite in a Holocene speleothem, Carsbad Caverns, New Mexico. Journal of Sedimentary Petrology 46, 486–496.

Folk, R.L., Pittmann, J.S., 1971. Length-slow chalcedony: A new testament for vanished evaporites. Journal of Sedimentary Petrology 41, 1045–1058.

Foubert, A., Jaramillo-Vogel, D., Held, A.-E., Camoin, C., Virgone, A., 2014. Diagenesis of Cretaceous pre-salt deposits : Namibe and Benguela Basins (Angola). Fribourg, Switzerland.

Fouke, B.W., 2011. Hot-spring Systems Geobiology: abiotic and biotic influences on travertine formation at Mammoth Hot Springs, Yellowstone National Park, USA. Sedimentology 58, 170–219. doi:10.1111/j.1365-3091.2010.01209.x

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Fouke, B.W., Bonheyo, G.T., Sanzenbacher, B., Frias-lopez, J., 2003. Partitioning of bacterial communities between travertine depositional facies at Mammoth Hot Springs, Yellowstone National Park, USA. Canadian Journal of Earth Sciences 40, 1531–1548. doi:10.1139/E03-067

Fouke, B.W., Farmer, J.D., Marais, D.J. Des, Pratt, L., Sturchio, N.C., Burns, P.C., Discipulo, M.K., 2000. Depositional facies and aqueous-solid geochemistry of travertine-depositing hot springs (Angel Terrace, Mammoth Hot Springs, Yellowstone National Park, U.S.A.). Journal of sedimentary research. Section A, Sedimentary petrology and processes : an international journal of SEPM (Society for Sedimentary Geology) 70, 565–85.

Frantz, C.M., Petryshyn, V.A., Marenco, P.J., Tripati, A., Berelson, W.M., Corsetti, F.A., 2014. Dramatic local environmental change during the early eocene climatic optimum detected using high resolution chemical analyses of Green River Formation stromatolites. Palaeogeography, Palaeoclimatology, Palaeoecology 405, 1–15. doi:10.1016/j.palaeo.2014.04.001

Freytet, P., Plaziat, J.C., 1982. Continental carbonate sedimentation and pedogenesis - Late Cretaceous and Early Tertiary of Southern France, 12th ed, Contributions to Sedimentology. Schweizerbart’sche Verlag, Stuttgart.

Freytet, P., Verrecchia, E., 1995. Discovery of Ca Oxalate Crystals Associated with Fungi in Moss Travertines (Bryoherms, Fresh-Water Heterogeneous Stromatolites). Geomicrobiology Journal 13, 117–127. doi:10.1080/01490459509378010

Freytet, P., Verrecchia, E.., 1999. Calcitic radial palisadic fabric in freshwater stromatolites: diagenetic and recrystallized feature or physicochemical sinter crust? Sedimentary Geology 126, 97–102. doi:10.1016/S0037-0738(99)00034-2

Freytet, P., Verrecchia, E.P., 2002. Lacustrine and palustrine carbonate petrography: An overview. Journal of Paleolimnology 27, 221–237. doi:10.1023/A:1014263722766

ACCEPTED MANUSCRIPT

Freytet, P., Verrecchia, E.P., 1998. Freshwater organisms that build stromatolites : a synopsis of biocrystallization by prokaryotic and eukaryotic algae. Sedimentology 45, 535–563.

Frisia, S., 2015. Microstratigraphic logging of calcite fabrics in speleothems as tool for palaeoclimate studies. International Journal of Speleology 44, 1–16. doi:10.5038/1827-806X.44.1.1

Frisia, S., 1996. Petrographic evidences of diagenesis in speleothems: some examples. Spéléochronos 7, 21–30.

Frisia, S., Borsato, A., 2010. Karst. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds.), Carbonates in Continental Settings: Facies, Environments and Processes. Developments in Sedimentology 61. Elsevier B.V., Amsterdam, pp. 269–318.

Frisia, S., Borsato, A., Fairchild, I.J., Mcdermott, F., Selmo, E.M., 2002. Aragonite–Calcite Relationships in Speleothems (Grotte De Clamouse, France): Environment, Fabrics, and Carbonate Geochemistry. Journal of Sedimentary Research 72, 687–699. doi:10.1306/020702720687

Gabitov, R.I., Watson, E.B., Sadekov, A., 2012. Oxygen isotope fractionation between calcite and fluid as a function of growth rate and temperature: An in situ study. Chemical Geology 306–307, 92–102. doi:10.1016/j.chemgeo.2012.02.021

Gandin, A., Capezzuoli, E., 2014. Travertine: Distinctive depositional fabrics of carbonates from thermal spring systems. Sedimentology 61, 264–290.

Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E.A., Schrag, D., Eiler, J.M., 2006. 13C–18O bonds in carbonate minerals: a new kind of paleothermometer. Geochimica et Cosmochimica Acta 70, 1439–1456. doi:10.1016/j.gca.2005.11.014

Golubić, S., Violante, C., Plenković-Moraj, A., Grgasović, T., 2008. Travertines and calcareous tufa deposits: an insight into diagenesis. Geologia Croatica 61, 363–378.

Gradzinski, M., 2010. Factors controlling gorwth of modern tufa: results of a field experiment. In:

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Pedley, H.M., Rogerson, M. (Eds.), Tufas and Speleothems: Unravelling the Microbial and Physical Controls. Geological Society, London, pp. 143–192.

Graustein, W.C., Cromack, K., Sollins, P., 1977. Calcium oxalate: Occurrence in soils and effect on nutrient and geochemical cycles. Science 198, 1252 – 1254.

Gregg, J.M., Bish, D.L., Kaczmarek, S.E., Machel, H.G., 2015. Mineralogy, nucleation and growth of dolomite in the laboratory and sedimentary environment: A review. Sedimentology 62, 1749–1769. doi:10.1111/sed.12202

Guo, L., Riding, R., 1999. Rapid facies changes in Holocene fissure ridge hot spring travertines, Rapolano Terme, Italy. Sedimentology 46, 1145–1158. doi:10.1046/j.1365-3091.1999.00269.x

Guo, L., Riding, R., 1998. Hot-spring travertine facies and sequences, Late Pleistocene, Rapolano Terme, Italy. Sedimentology 45, 163–180.

Guo, L., Riding, R., 1994. Origin and diagenesis of Quaternary travertine shrub fabrics, Rapolano Terme, eastern Italy. Sedimentology 41, 499–520.

Guo, L., Riding, R., 1992. Aragonite laminae in hot water travertine crusts, Rapolano Terme, Italy. Sedimentology 39, 1067–1079. doi:10.1111/j.1365-3091.1992.tb01997.x

Hardie, L.A., 1987. Dolomitization: A critical review of some current views. Journal of Sedimentary Petrology 57, 166–183.

Harris, N.B., 2000. Toca carbonate, Congo Basin: response to an evolving Rift Lake. AAPG Memoir 73 73, 341–360.

Hoefs, J., 2004. Stable isotope geochemistry. Springer-Verlag Berlin Heidelberg.

Horner, H.T., Wagner, B.L., 1995. Calcium oxalate formation in higher plants. In: Khan, S.R. (Ed.), Calcium Oxalate in Biological Systems. CRC, Boca Raton, pp. 53–72.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Hu, Y. Bin, Wolf-Gladrow, D.A., Dieckmann, G.S., Völker, C., Nehrke, G., 2014. A laboratory study of ikaite ($CaCO_3.6H_2O$) precipitation as a function of pH, salinity, temperature and phosphate concentration. Marine Chemistry 162, 10–18. doi:10.1016/j.marchem.2014.02.003

Huntington, K.W., Budd, D.A., Wernicke, B.P., Eiler, J.M., 2006. Use of clumped-isotope thermometry to constrain the crystallization temperature of diagenetic calcitee. Journal of Sedimentary Research 81, 656–669. doi:10.2110/jsr.2011.51

Immenhauser, A., Buhl, D., Richter, D., Niedermayr, A., Riechelmann, D., Dietzel, M., Schulte, U., 2010. Magnesium-isotope fractionation during low-Mg calcite precipitation in a limestone cave - Field study and experiments. Geochimica et Cosmochimica Acta 74, 4346–4364. doi:10.1016/j.gca.2010.05.006

Inverarity, K., Heinson, G., Hatch, M., 2016. Groundwater flow underneath mound spring tufas from geophysical surveys in the southwestern Great Artesian Basin, Australia. Australian Journal of Earth Sciences 63, 857–872. doi:10.1080/08120099.2016.1261942

James, N.P., Choquette, P.W., 1984. Diagenesis 9. Limestones-the meteoric diagenetic environment. Geoscience Canada 11, 161–194.

James, N.P., Jones, B., 2015. Origin of Carbonate Sedimentary Rocks. Wiley.

Janssen, A., Swennen, R., Podoor, N., Keppens, E., 1999. Biological and diagenetic influence in Recent and fossil tufa deposits from Belgium. Sedimentary Geology 126, 75–95. doi:10.1016/S0037-0738(99)00033-0

Jaramillo-Vogel, D., Schaegis, J.C., Perrochet, L., Atnafu, B., Kidane, T., Foubert, A., 2016. Diagenetic transformation of isopachous laminated fibrous aragonite into irregular laminated peloidal calcite fabrics (Danakil Depression, Ethiopia). In: Tomás, S., Christ, N., Mutti, M. (Eds.), The Dolomieu Conference on Carbonate Platforms and Dolomite. Selva di Val Gardena, Italy, p. 74.

ACCEPTED MANUSCRIPT

Jones, B., 2017. Review of calcium carbonate polymorph precipitation in spring systems. Sedimentary Geology 353, 64–75. doi:10.1016/j.sedgeo.2017.03.006

Jones, B., 2010. Microbes in caves: agens of calcite corrosion and precipitation. In: Pedley, H.M., Rogerson, M. (Eds.), Tufas and Speleothems: Unravelling the Microbial and Physical Controls. Geological Society of London, Special Publication no. 336, London, pp. 7–30.

Jones, B., Peng, X., 2012a. Amorphous calcium carbonate associated with biofilms in hot spring deposits. Sedimentary Geology 269–270, 58–68. doi:10.1016/j.sedgeo.2012.05.019

Jones, B., Peng, X., 2012b. Intrinsic versus extrinsic controls on the development of calcite dendrite bushes, Shuzhishi Spring, Rehai geothermal area, Tengchong, Yunnan Province, China. Sedimentary Geology 249, 45–62. doi:10.1016/j.sedgeo.2012.01.009

Jones, B., Renaut, R.W., 2010. Calcareous Spring Deposits in Continental Settings. In: Alonso-Zarza, A.M., Tanner, L. (Eds.), Carbonates in Continental Settings. Elsevier, Amsterdam, pp. 177–224. doi:10.1016/S0070-4571(09)06104-4

Jones, B., Renaut, R.W., 2008. Cyclic development of large, complex, calcite dendrite crystals in the Clinton travertine, Interior British Columbia, Canada. Sedimentary Geology 203, 17–35. doi:10.1016/j.sedgeo.2007.10.002

Jones, B.F., 1986. Clay Mineral Diagenesis in Lacustrine Sediments. In: Mumpton, F.A. (Ed.), Studies in Diagenesis. US Geological Survey, pp. 291–300.

Kahle, C.F., 1977. Origin of subaerial Holocene calcareous crusts: role of algae, fungi and sparmicritization. Sedimentology 24, 413–435.

Kandianis, M.T., Fouke, B.W., Johnson, R.W., Veysey, J., Inskeep, W.P., 2008. Microbial biomass: A catalyst for $CaCO_3$ precipitation in advection-dominated transport regimes. Geological Society of America Bulletin 120, 442–450. doi:10.1130/B26188.1

ACCEPTED MANUSCRIPT

Kanellopoulos, C., 2013. Various morphological types of thermogenic travertines in northern Euboea and Eastern Central Greece. Bulletin of the Geological Society of Greece XLVII, 1929–1938.

Kanellopoulos, C., 2012. Distribution, lithotypes and mineralogical study of newly formed thermogenic travertines in Northern Euboea and Eastern Central Greece. Open Geosciences 4, 545–560. doi:10.2478/s13533-012-0105-z

Kanellopoulos, C., Christopoulou, M., Xenakis, M., Vakalopoulos, P., 2016. Hydrochemical characteristics and geothermy applications of hot groundwater in the Edipsos area, NW Euboea (Evia), Greece. Bulletin of the Geological Society of Greece XLV, 1–10.

Kawai, T., Kano, A., Hori, M., 2009. Geochemical and hydrological controls on biannual lamination of tufa deposits. Sedimentary Geology 213, 41–50. doi:10.1016/j.sedgeo.2008.11.003

Kele, S., Breitenbach, S.F.., Capezzuoli, E., Meckler, A.N., Ziegler, M., Millan, I.M., Kluge, T., Deák, J., Hanselmann, K., John, C.M., Yan, H., Liu, Z., Bernasconi, S.M., 2015. Temperature dependence of oxygen- and clumped isotope fractionation in carbonates: A study of travertines and tufas in the 6-95°C temperature range. Geochimica et Cosmochimica Acta 168, 172–192. doi:10.1016/j.gca.2015.06.032

Kele, S., Demény, A., Siklósy, Z., Németh, T., Tóth, M., Kovács, M.B., 2008. Chemical and stable isotope composition of recent hot-water travertines and associated thermal waters, from Egerszalók, Hungary: Depositional facies and non-equilibrium fractionation. Sedimentary Geology 211, 53–72. doi:10.1016/j.sedgeo.2008.08.004

Kele, S., Özkul, M., Fórizs, I., Gökgöz, A., Baykara, M.O., Alçiçek, M.C., Németh, T., 2011. Stable isotope geochemical study of Pamukkale travertines: New evidences of low-temperature non-equilibrium calcite-water fractionation. Sedimentary Geology 238, 191–212. doi:10.1016/j.sedgeo.2011.04.015

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Kelson, J.R., Huntington, K.W., Schauer, A.J., Saenger, C., Lechler, A.R., 2017. Toward a universal carbonate clumped isotope calibration: Diverse synthesis and preparatory methods suggest a single temperature relationship. Geochimica et Cosmochimica Acta 197, 104–131. doi:10.1016/j.gca.2016.10.010

Kendall, A.C., Iannace, A., 2001. “Sediment”-cement relationships in a Pleistocene speleothem from Italy: A possible analogue for “replacement” cements and Archaeolithoporella in ancient reefs. Sedimentology 48, 681–698. doi:10.1046/j.1365-3091.2001.00391.x

Kharaka, Y.K., Sorey, M.L., Thordsen, J.J., 2000. Large-scale hydrothermal fluid discharges in the Norris–Mammoth corridor, Yellowstone National Park, USA. Journal of Geochemical Exploration 69–70, 201–205. doi:10.1016/S0375-6742(00)00025-X

Kluge, T., Affek, H.P., 2012. Quantifying kinetic fractionation in Bunker Cave speleothems using D47. Geochimica et Cosmochimica Acta 49, 82–94.

Kluge, T., Affek, H.P., Zhang, Y.G., Dublyansky, Y., Spötl, C., Immenhauser, A., Richter, D.K., 2014. Clumped isotope thermometry of cryogenic cave carbonates. Geochimica et Cosmochimica Acta 126, 541–554. doi:10.1016/j.gca.2013.11.011

Knoll, A.H., Worndle, S., Kah, L.C., 2013. Covariance of Microfossil Assemblages and Microbialite Textures Across an Upper Mesoproterozoic Carbonate Platform. Palaios 28, 453–470. doi:10.2110/palo.2013.p13-005r

Koch, R., Rothe, P., 1985. Recent Meteoric Diagenesis of Miocene Mg-Calcite (Hydrobia Beds, Mainz Basin, Germany). Facies 13, 271–285.

Kolo, K., Keppens, E., Préat, A., Claeys, P., 2007. Experimental observations on fungal diagenesis of carbonate substrates. Journal of Geophysical Research Biogeosciences 112, GO1007.

Krause, S., Liebetrau, V., Gorb, S., Sánchez-Román, M., McKenzie, J.A., Treude, T., 2012. Microbial

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

nucleation of Mg-rich dolomite in exopolymeric substances under anoxic modern seawater salinity: New insight into an old enigma. Geology 40, 587–590. doi:10.1130/G32923.1

Kremer, B., Kazmierczak, J., Łukomska-Kowalczyk, M., Kempe, S., 2012. Calcification and Silicification: Fossilization Potential of Cyanobacteria from Stromatolites of Niuafo"ou"s Caldera Lakes (Tonga) and Implications for the Early Fossil Record. Astrobiology 12, 535–548. doi:10.1089/ast.2011.0742

Kunzler, R.H., Goodell, H.G., 1970. The aragonite-calcite transformation; a problem in the kinetics of a solid-solid reaction. American Journal of Science 269, 360–391. doi:10.2475/ajs.269.4.360

Lachniet, M.S., Bernal, J.P., Asmerom, Y., Polyak, V., 2012. Uranium loss and aragonite-calcite age discordance in a calcitized aragonite stalagmite. Quaternary Geochronology 14, 26–37. doi:10.1016/j.quageo.2012.08.003

Lebatard, A.-E., Alçiçek, M.C., Rochette, P., Khatib, S., Vialet, A., Boulbes, N., Bourlès, D.L., Demory, F., Guipert, G., Mayda, S., Titov, V. V., Vidal, L., Lumley, H. de, 2014. Dating the *Homo erectus* bearing travertine from Kocabaş (Denizli, Turkey) at at least 1.1 Ma. Earth and Planetary Science Letters 390, 8–18. doi:10.1016/j.epsl.2013.12.031

Lécuyer, C., Reynard, B., Martineau, F., 2004. Stable isotope fractionation between mollusc shells and marine waters from Martinique Island. Chemical Geology 213, 293–305.

Lindsay, M.R., Anderson, C., Fox, N., Scofield, G., Allen, J., Anderson, E., Bueter, L., Poudel, S., Sutherland, K., Munson-McGee, J.H., Nostrand, J.D. Van, Zhou, J., Spear, J.R., Baxter, B.K., Lageson, D.R., Boyd, E.S., 2017. Microbialite response to an anthropogenic salinity gradient in Great Salt Lake, Utah. Geobiology 15, 131–145.

Lohmann, K.C., 1988. Geochemical patterns of meteoric diagenetic systems and their application to studies of paleokarst. In: James, N.P., Choquette, P.W. (Eds.), Paleokarst. Springer-Verlag, New

ACCEPTED MANUSCRIPT

York, pp. 58–78.

Longman, M.W., 1980. Carbonate diagenetic textures from near surface diagenetic environments. AAPG Bulletin 64, 461–487.

Lopez, B., Camoin, G., Özkul, M., Swennen, R., Virgone, A., 2017. Sedimentology of coexisting travertine and tufa deposits in a mounded geothermal spring carbonate system, Obruktepe, Turkey. Sedimentology 64, 903–931. doi:10.1111/sed.12284

Love, K.M., Chafetz, H.S., 1988. Diagenesis of laminated travertine crusts, Arbuckle Mountains, Oklahoma. Journal of Sedimentary Research 58, 441–445. doi:10.1306/212F8DB4-2B24-11D7-8648000102C1865D

Machel, H.G., 2004. Concepts and models of dolomitization: a critical reappraisal. Geological Society 235, 7–63. doi:10.1144/GSL.SP.2004.235.01.02

Malesani, P., Vannucchi, S., 1975. Precipitazione di calcite o i aragonite dalle acque termominerale in relazione alla genesi e all'evoluzione dei travertini. Atti dell R. Academia d'Italia 58, 761–766.

Martignier, A., Pacton, M., Filella, M., Jaquet, J.M., Barja, F., Pollok, K., Langenhorst, F., Lavigne, S., Guagliardo, P., Kilburn, M.R., Thomas, C., Martini, R., Ariztegui, D., 2017. Intracellular amorphous carbonates uncover a new biomineralization process in eukaryotes. Geobiology 15, 240–253. doi:10.1111/gbi.12213

Martín-García, R., Alonso-Zarza, A.M., Martín-Pérez, A., 2009. Loss of primary texture and geochemical signatures in speleothems due to diagenesis: Evidences from Castañar Cave, Spain. Sedimentary Geology 221, 141–149. doi:10.1016/j.sedgeo.2009.09.007

Martín-García, R., Alonso-Zarza, A.M., Martín-Pérez, A., Schröder-Ritzrau, A., Ludwig, T., 2014. Relationships between colour and diagenesis in the aragonite-calcite speleothems in Basajaún Etxea cave, Spain. Sedimentary Geology 312, 63–75. doi:10.1016/j.sedgeo.2014.08.001

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Martín-García, R., Martín-Pérez, A., Alonso-Zarza, A.M., 2011. Weathering of host rock and corrosion over speleothems in Castañar cave, Spain: An example of a complex meteoric environment. Carbonates and Evaporites 26, 83–94. doi:10.1007/s13146-010-0039-9

Martín-Pérez, A., Alonso-Zarza, A.M., Iglesia, A. La, Martín-García, R., 2015a. Do magnesian clays play a role in dolomite formation in alkaline environments? An example from Castañar Cave, Cáceres (Spain). Geogaceta 57, 15–18.

Martín-Pérez, A., Košir, A., 2017. Biogenicity of fibrous microcrystalline calcite in vadose terrestrial settings. In: Lyell Meeting 2017: Sticking Together: Microbes and Their Role in Forming Sediments. The Geological Society of London, London, UK, p. 87.

Martín-Pérez, A., Košir, A., Otoničar, B., 2015b. Dolomite in speleothems of Snežna Jama, Slovenia. Acta Carsologica 44, 81–100.

Martín-Pérez, A., Martín-García, R., Alonso-Zarza, A.M., 2012. Diagenesis of a drapery speleothem from Castañar Cave: From dissolution to dolomitization. International Journal of Speleology 41, 251–266. doi:10.5038/1827-806X.41.2.11

Melezhik, V.A., Fallick, A.E., 2001. Palaeoproterozoic travertines of volcanic affiliation from a C-13-rich rift lake environment. Chemical Geology 173, 293–312. doi:10.1016/S0009-2541(00)00281-3

Melim, L. a., Spilde, M.N., 2011. Rapid Growth and Recrystallization of Cave Pearls In An Underground Limestone Mine. Journal of Sedimentary Research 81, 775–786. doi:10.2110/jsr.2011.65

Mercedes-Martín, R., Brasier, A., Rogerson, M., Reijmer, J., Vonhof, H., Pedley, M., 2017. A depositional model for spherulitic carbonates associated with alkaline, volcanic lakes. Journal of Marine and Petroleum Geology in press. doi:10.1016/j.marpetgeo.2017.05.032

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Mercedes-Martín, R., Rogerson, M.R., Brasier, A.T., Vonhof, H.B., Prior, T.J., Fellows, S.M., Reijmer, J.J.G., Billing, I., Pedley, H.M., 2016. Growing spherulitic calcite grains in saline, hyperalkaline lakes: Experimental evaluation of the effects of Mg-clays and organic acids. Sedimentary Geology 335, 93–102. doi:10.1016/j.sedgeo.2016.02.008

Mettraux, M., Homewood, P., Anjos, C. Dos, Erthal, M., Lima, R., Matsuda, N., Souza, A., Balushi, S. Al, 2015. Microbial communities and their primary to early diagenetic mineral phases; the record from Neoproterozoic microbialites of Qarn Alam, Oman. In: Bosence, D.W.J., Gibbons, K.A., Heron, D.P. Le, Morgan, W.Q., Pritchard, T., Vining, B.A. (Eds.), Microbial Carbonates in Space and Time: Implications for Global Exploration and Porduction. Geological Society of London, Special Publication 418, London, UK, pp. 123–154. doi:10.1144/SP418.5

Meyers, W.J., Lohmann, K.C., 1985. Isotope geochemistry of regionally extensive calcite cement zones and marine components in Mississippian limestones, New Mexico. In: Carbonate Cements (SP36). SEPM, pp. 223–239.

Michaelis, W., Seifert, R., Nauhaus, K., Treude, T., Thiel, V., Blumenberg, M., Knittel, K., Gieseke, A., Peterknecht, K., Pape, T., Boetius, A., Amann, R., Jørgensen, B.B., Widdel, F., Peckmann, J.R., Pimenov, N. V, Gulin, M.B., 2002. Microbial reefs in the Black Sea fueled by anaerobic oxidation of methane. Science 297, 1013–1015.

Milliere, L., Hasinger, O., Bindschedler, S., Cailleau, G., Spangenberg, J.E., Verrecchia, E.P., 2011. Stable carbon and oxygen isotope signatures of pedogenic needle fibre calcite. Geoderma 161, 74–87. doi:10.1016/j.geoderma.2010.12.009

Millière, L., Spangenberg, J.E., Bindschedler, S., Cailleau, G., Verrecchia, E.P., 2011. Reliability of stable carbon and oxygen isotope compositions of pedogenic needle fibre calcite as environmental indicators: examples from Western Europe. Isotopes in Environmental and Health Studies 47, 341–358. doi:10.1080/10256016.2011.601305

ACCEPTED MANUSCRIPT

Minissale, A., Kerrick, D.M., Magro, G., Murrell, M.T., Paladini, M., Rihs, S., Sturchio, N.C., Tassi, F., Vaselli, O., 2002. Geochemistry of Quaternary travertines in the region north of Rome (Italy): Structural, hydrologic and paleoclimatic implications. Earth and Planetary Science Letters 203, 709–728. doi:10.1016/S0012-821X(02)00875-0

Moore, C.H., 2001. Carbonate Reservoirs. Porosity Evolution and Diagenesis in a Sequence Stratigraphic Framework. Developments in Sedimentology, 55. Elsevier, Amsterdam.

Moore, C.H., Wade, W.J., 2013. Carbonate Reservoirs. Porosity and Diagenesis in a Sequence Stratigraphic Framework, 2nd ed. Elsevier, Amsterdam.

Morse, J.W., Mackenzie, F.T., 1990. Geochemistry of sedimentary carbonates. Developments in Sedimentology 48. Elsevier, Amsterdam. doi:10.1016/0016-7037(93)90401-H

Nielsen, M.H., Aloni, S., Yoreo, J.J. De, 2014. In situ TEM imaging of $CaCO_3$ nucleation reveals coexistence of direct and indirect pathways. Science 345, 1158–1162. doi:10.1126/science.1254051

Noten, K. Van, Claes, H., Soete, J., Foubert, A., Özkul, M., Swennen, R., 2013. Fracture networks and strike–slip deformation along reactivated normal faults in Quaternary travertine deposits, Denizli Basin, western Turkey. Tectonophysics 588, 154–170. doi:10.1016/j.tecto.2012.12.018

Nutman, A.P., Bennett, V.C., Friend, C.R.L., Kranendonk, M.J. Van, Chivas, A.R., 2016. Rapid emergence of life shown by discovery of 3,700-million-year-old microbial structures. Nature 537, 1–12. doi:10.1038/nature19355

Oehler, D.Z., Robert, F., Walter, M.R., Sugitani, K., Allwood, A., Meibom, A., Mostefaoui, S., Selo, M., Thomen, A., Gibson, E.K., 2009. NanoSIMS: Insights to biogenicity and syngeneity of Archaean carbonaceous structures. Precambrian Research 173, 70–78. doi:10.1016/j.precamres.2009.01.001

ACCEPTED MANUSCRIPT

Okumura, T., Takashima, C., Kano, A., 2013. Textures and processes of laminated travertines formed by unicellular cyanobacteria in myoken hot spring, southwestern Japan. Island Arc 22, 410–426. doi:10.1111/iar.12034

Owen, R.A., Day, C.C., Hu, C.Y., Liu, Y.H., Pointing, M.D., Blättler, C.L., Henderson, G.M., 2016. Calcium isotopes in caves as a proxy for aridity: Modern calibration and application to the 8.2 kyr event. Earth and Planetary Science Letters 443, 129–138. doi:10.1016/j.epsl.2016.03.027

Özkul, M., Kele, S., Gökgöz, A., Shen, C.-C., Jones, B., Baykara, M.O., Fórizs, I., Németh, T., Chang, Y.-W., Alçiçek, M.C., 2013. Comparison of the Quaternary travertine sites in the Denizli extensional basin based on their depositional and geochemical data. Sedimentary Geology 294, 179–204. doi:10.1016/j.sedgeo.2013.05.018

Pace, A., Bourillot, R., Bouton, A., Vennin, E., Galaup, S., Bundeleva, I., Patrier, P., Dupraz, C., Thomazo, C., Sansjofre, P., Yokoyama, Y., Franceschi, M., Anguy, Y., Pigot, L., Virgone, A., Visscher, P.T., 2016. Microbial and diagenetic steps leading to the mineralisation of Great Salt Lake microbialites. Scientific reports 6, 31495. doi:10.1038/srep31495

Pache, M., Reitner, J., Arp, G., 2001. Geochemical evidence for the formation of a large Miocene “travertine” mound at a sublacustrine spring in a soda lake (Wallerstein castle rock, Nördlinger Ries, Germany). Facies 45, 211–230. doi:10.1007/BF02668114

Patterson, W.P., Smith, G.R., Lohmann, K.C., 1993. Continental paleothermometry and seasonality using the isotopic composition of aragonitic otoliths of freshwater fishes. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), Climate Change in Continental Isotopic Records. pp. 191–202. doi:10.1029/GM078p0191

Pedley, H.M., Rogerson, M. (Eds.), 2010. Tufas and Speleothems - Unravelling the Microbial and Physical Controls, Geological. ed. Geological Society of London.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Pedley, M., 2014. The morphology and function of thrombolitic calcite precipitating biofilms: A universal model derived from freshwater mesocosm experiments. Sedimentology 61, 22–40. doi:10.1111/sed.12042

Pedley, M., 2009. Tufas and travertines of the Mediterranean region: A testing ground for freshwater carbonate concepts and developments. Sedimentology 56, 221–246. doi:10.1111/j.1365-3091.2008.01012.x

Pedone, V. a., Dickson, J. a. D., 2000. Replacement of Aragonite by Quasi-Rhombohedral Dolomite in a Late Pleistocene Tufa Mound, Great Salt Lake, Utah, U.S.A. Journal of Sedimentary Research 70, 1152–1159. doi:10.1306/041200701152

Peng, X., Jones, B., 2013. Patterns of biomediated $CaCO_3$ crystal bushes in hot spring deposits. Sedimentary Geology 294, 105–117. doi:10.1016/j.sedgeo.2013.05.009

Pentecost, A., 2005. Travertine. Springer-Verlag Berlin Heidelberg.

Pentecost, A., 1995. The Quaternary travertine deposits of Europe and Asia minor. Quaternary Science Reviews 14, 1005–1028. doi:0277-3791/95 00101-4

Pentecost, A., Bayari, S., Yesertener, C., 1997. Phototrophic Microorganisms of the Pamukkale Travertine, Turkey: Their Distribution and Influence on Travertine Deposition. Geomicrobiology Journal 14, 269–283.

Philips, S.E., Milness, A.R., Foster, R.C., 1987. Calcified filaments : an example of biological influences in the formation of calcrete in South Australia. Australian Journal of Soil Research 25, 405–428.

Plee, K., 2008. Geomicrobiological investigation of ooid cortex formation in a freshwater environment – Lake Geneva, Switzerland (Unpublished PhD Thesis). University of Geneva.

Porta, G. Della, 2015. Carbonate build-ups in lacustrine, hydrothermal and fluvial settings: comparing depositinoal geometry, fabric types and geochemical signature. In: Bosence, D.W.J., Gibbons,

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

K.A., Heron, D.P. Le, Morgan, W.Q., Pritchard, T., Vining, B.A. (Eds.), Microbial Carbonates in Space and Time: Implications for Global Exploration and Porduction. Geological Society of London, Special Publications 418, pp. 17–68.

Porta, G. Della, Capezzuoli, E., Bernardo, A. De, 2017. Facies character and depositional architecture of hydrothermal travertine slope aprons (Pleistocene, Acquasanta Terme, Central Italy). Marine and Petroleum Geology 1–17. doi:10.1016/j.marpetgeo.2017.03.014

Purgstaller, B., Mavromatis, V., Immenhauser, A., Dietzel, M., 2016. Transformation of Mg-bearing amorphous calcium carbonate to Mg-calcite - In situ monitoring. Geochimica et Cosmochimica Acta 174, 180–195. doi:10.1016/j.gca.2015.10.030

Radha, A.V., Forbes, T.Z., Killian, C.E., Gilbert, P.U.P.A., Navrotsky, A., 2010. Transformation and crystallization energetics of synthetic and biogenic amorphous calcium carbonate. Proceedings of the National Academy of Sciences of the United States of America 107, 16438–16443. doi:10.1073/pnas.1009959107

Railsback, L.B., Dabous, A.A., Osmond, J.K., Fleisher, C.J., 2002. Petrographic and geochemical screening of speleothems for U-series dating: An example from recrystallized speleothems from Wadi Sannur Cavern, Egypt. Journal of Cave and Karst Studies 64, 108–116.

Rainey, D.K., Jones, B., 2007. Rapid cold water formation and recrystallization of relict bryophyte tufa at the Fall Creek cold springs, Alberta, Canada. Canadian Journal of Earth Sciences 44, 889–909. doi:10.1139/E07-008

Renaut, R.W., Jones, B., 1997. Controls on Aragonite and Calcite Precipitation in Hot Spring Travertines at Chemurkeu, Lake Bogoria, Kenya. Canadian Journal of Earth Sciences 34, 801–818.

Renaut, R.W., Owen, R.B., Jones, B., Tiercelin, J.J., Tarits, C., Ego, J.K., Konhauser, K.O., 2013. Impact

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

of lake-level changes on the formation of thermogene travertine in continental rifts: Evidence from Lake Bogoria, Kenya Rift Valley. Sedimentology 60, 428–468. doi:10.1111/j.1365-3091.2012.01347.x

Richter, D.K., Heinrich, F., Geske, A., Neuser, R.D., Gies, H., Immenhauser, A., 2014. First description of Phanerozoic radiaxial fibrous dolomite. Sedimentary Geology 304, 1–10. doi:10.1016/j.sedgeo.2014.02.002

Riding, R., 1979. Origin and diagenesis of lacustrine algal bioherms at the margin of the Ries crater, Upper Miocene, southern Germany. Sedimentology 26, 645–680.

Riechelmann, D.F.C., Deininger, M., Scholz, D., Riechelmann, S., Schröder-Ritzrau, A., Spötl, C., Richter, D.K., Mangini, A., Immenhauser, A., 2013. Disequilibrium carbon and oxygen isotope fractionation in recent cave calcite: Comparison of cave precipitates and model data. Geochimica et Cosmochimica Acta 103, 232–244. doi:10.1016/j.gca.2012.11.002

Riechelmann, S., Buhl, D., Schröder-Ritzrau, A., Riechelmann, D.F.C., Richter, D.K., Vonhof, H.B., Wassenburg, J.A., Geske, A., Spötl, C., Immenhauser, A., 2012. The magnesium isotope record of cave carbonate archives. Climate of the Past 8, 1849–1867. doi:10.5194/cp-8-1849-2012

Riechelmann, S., Schröder-Ritzrau, A., Wassenburg, J.A., Schreuer, J., Richter, D.K., Riechelmann, D.F.C., Terente, M., Constantin, S., Mangini, A., Immenhauser, A., 2014. Physicochemical characteristics of drip waters: Influence on mineralogy and crystal morphology of recent cave carbonate precipitates. Geochimica et Cosmochimica Acta 145, 13–29. doi:10.1016/j.gca.2014.09.019

Ritter, A.C., Kluge, T., Berndt, J., Richter, D.K., John, C.M., Bodin, S., Immenhauser, A., 2015. Application of redox sensitive proxies and carbonate clumped isotopes to Mesozoic and Palaeozoic radiaxial fibrous calcite cements. Chemical Geology 417, 306–321. doi:10.1016/j.chemgeo.2015.10.008

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Ritter, A.C., Mavromatis, V., Dietzel, M., Kwiecien, O., Wiethoff, F., Griesshaber, E., Casella, L.A., Schmahl, W.W., Koelen, J., Neuser, R.D., Leis, A., Buhl, D., Niedermayr, A., Breitenbach, S.F.M., Bernasconi, S.M., Immenhauser, A., 2017. Exploring the impact of diagenesis on (isotope) geochemical and microstructural alteration features in biogenic aragonite. Sedimentology 64, 1354–1380. doi:10.1111/sed.12356

Roberts, J.A., Kenward, P.A., Fowle, D.A., Goldstein, R.H., González, L.A., Moore, D.S., 2013. Surface chemistry allows for abiotic precipitation of dolomite at low temperature. Proceedings of the National Academy of Sciences of the United States of America 110, 14540–5. doi:10.1073/pnas.1305403110

Rodriguez-Blanco, J.D., Sand, K.K., Benning, L.G., 2017. Chapter 5: ACC and Vaterite as Intermediates in the Solution-Based Crystllization of $CaCO_3$. In: Driessche, A. van, Kellermeier, M., Benning, L.G., Gebauer, D. (Eds.), New Perspectives on Mineral Nucleation and Growth. From Solution Precursors to Solid Material. Springer International Publishing Switzerland, pp. 93–111.

Rodriguez-Blanco, J.D., Shaw, S., Benning, L.G., 2011. The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite, via vaterite. Nanoscale 3, 265–271. doi:10.1039/c0nr00589d

Rodriguez-Blanco, J.D., Shaw, S., Bots, P., Roncal-Herrero, T., Benning, L.G., 2012. The role of pH and Mg on the stability and crystallization of amorphous calcium carbonate. Journal of Alloys and Compounds 536, S477–S479. doi:10.1016/j.jallcom.2011.11.057

Rogerson, M., Mercedes-Martín, R., Brasier, A.T., McGill, R.A.R., Prior, T.J., Vonhof, H., Fellows, S.M., Reijmer, J.J.G., McClymont, E., Billing, I., Matthews, A., Pedley, H.M., 2017. Are spherulitic lacustrine carbonates an expression of large-scale mineral carbonation? A case study from the East Kirkton Limestone, Scotland. Gondwana Research 48, 101–109. doi:10.1016/j.gr.2017.04.007

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Rogerson, M., Pedley, H.M., Kelham, A., Wadhawan, J.D., 2014. Linking mineralisation process and sedimentary product in terrestrial carbonates using a solution thermodynamic approach. Earth Surface Dynamics 2, 197–216. doi:10.5194/esurf-2-197-2014

Romanek, C.S., Grossman, E.L., Morse, J.W., 1992. Carbon isotopic fractionation in syntetic aragonite and calcite: effects of temperature and precipitation rate. Geochimica et Cosmochimica Acta 56, 419–430.

Ronchi, P., Cruciani, F., 2015. Continental carbonates as a hydrocarbon reservoir, an analog case study from the travertine of Saturnia, Italy. AAPG Bulletin 99, 711–734. doi:10.1306/10021414026

Rozanski, K., Araguás-Araguás, L., Gonfiantini, R., 1993. Isotopic Patterns in Modern Global Precipitation. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), Climate Change in Continental Isotopic Records. American Geophysical Union, pp. 1–36.

Sample, J.C., Torres, M.E., Fisher, A., Hong, W.-L., Destrigneville, C., Defliese, W.F., Tripati, A.E., 2017. Geochemical constraints on the temperature and timing of carbonate formation and lithification in the Nankai Trough, NanTroSEIZE transect. Geochimica et Cosmochimica Acta 198, 92–114.

Sanchez-Moral, S., Canaveras, J.C., Laiz, L., Saiz-Jimenez, C., Bedoya, J., Luque, L., 2003. Biomediated Precipitation of Calcium Carbonate Metastable Phases in Hypogean Environments: A Short Review. Geomicrobiology Journal 20, 491–500. doi:10.1080/713851131

Sánchez-Pastor, N.M., Oehlerich, M., Astilleros, J.M.J.M., Kaliwoda, M., Mayr, C.C.C.C., Fernández-Díaz, L. Schmahl, W.W., Fernández-Díaz, L., Schmahl, W.W., 2016. Crystallization of ikaite and its pseudomorphic transformation into calcite: Raman spectroscopy evidence. Geochimica et Cosmochimica Acta 175, 271–281. doi:10.1016/j.gca.2015.12.006

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Sánchez-Román, M., Romanek, C.S., Fernández-Remolar, D.C., Sánchez-Navas, A., McKenzie, J.A., Pibernat, R.A., Vasconcelos, C., 2011. Aerobic biomineralization of Mg-rich carbonates: Implications for natural environments. Chemical Geology 281, 143–150. doi:10.1016/j.chemgeo.2010.11.020

Sandberg, P.A., 1975. New interpretations of Great Salt Lake ooids and of ancient non-skeletal carbonate mineralogy. Sedimentology 22, 497–537. doi:10.1111/j.1365-3091.1975.tb00244.x

Schneider, J., Campion-Alsumard, T. Le, 1999. Construction and destruction of carbonates by marine and freshwater cyanobacteria. European Journal of Phycology 34, 417–426. doi:10.1080/09670269910001736472

Scholz, D., Tolzmann, J., Hoffmann, D.L., Jochum, K.P., Spötl, C., Riechelmann, D.F.C., 2014. Diagenesis of speleothems and its effect on the accuracy of ^{230}Th/U-ages. Chemical Geology 387, 74–86. doi:10.1016/j.chemgeo.2014.08.005

Schroeder, S., Ibekwe, A., Saunders, M., Dixon, R., Fisher, A., Schröder, S., Ibekwe, A., Saunderes, M., Dixon, R., Fisher, A., 2016. Algal-microbial carbonates of the Namibe Basin (Albian, Angola): implications for microbial carbonate mound development in the South Atlantic. Petroleum Geoscience 22, 71–90.

Seard, C., Camoin, G., Rouchy, J.M., Virgone, A., 2013. Composition, structure and evolution of a lacustrine carbonate margin dominated by microbialites: Case study from the Green River formation (Eocene; Wyoming, USA). Palaeogeography, Palaeoclimatology, Palaeoecology 381–382, 128–144. doi:10.1016/j.palaeo.2013.04.023

Shaikh, A.M., Shearman, D.J., 1986. On ikaite and the morphology of its pseudomorphs. In: Geochemistry and Mineral Formation in the Earth Surface. Proceedings of the International Meeting “Geochemistry of the Earth Surface and Processes of Mineral Formation.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Sharp, Z., 2007. Principles of Stable Isotope Geochemistry. Pearson Education, Inc., NJ, USA.

Shearman, D.J., McGugan, A., Stein, C., Smith., A.J., 1989. Ikaite, $CaCO_3.6H_20$, precursor of the thinolites in the Quaternary tufas and tufa mounds of the Labontan and Mono Lake basins, western United States. Geological Society of America Bulletin 101, 913–917.

Shiraishi, F., Bissett, A., Beer, D. de, Reimer, A., Arp, G., 2008a. Photosynthesis, respiration and exopolymer calcium-binding in biofilm calcification (Westerhöfer and Deinschwanger Creek, Germany). Geomicrobiology Journal 25, 83–94. doi:Doi 10.1080/01490450801934888

Shiraishi, F., Reimer, A., Bissett, A., Beer, D. de, Arp, G., 2008b. Microbial effects on biofilm calcification, ambient water chemistry and stable isotope records in a highly supersaturated setting (Westerhöfer Bach, Germany). Palaeogeography, Palaeoclimatology, Palaeoecology 262, 91–106. doi:10.1016/j.palaeo.2008.02.011

Simkiss, K., Wilbur, K.M., 1989. Biomineralization : Cell Biology and Mineral Deposition. Academic Press Inc., San Diego, California.

Soete, J., Kleipool, L.M., Claes, H., Claes, S., Hamaekers, H., Kele, S., Özkul, M., Foubert, A., Reijmer, J.J.G., Swennen, R., 2015. Acoustic properties in travertines and their relation to porosity and pore types. Marine and Petroleum Geology 59, 320–335. doi:10.1016/j.marpetgeo.2014.09.004

Sorey, M.L., Colvard, E.M., 1997. Hydrologic investigations in the Mammoth Corridor, Yellowstone National Park and vicinity, U.S.A. Geothermics 26, 221–249. doi:10.1016/S0375-6505(96)00041-7

Souza-Egipsy, V., Wierzchos, J., Ascaso, C., Nealson, K.H., 2005. Mg-silica precipitation in fossilization mechanisms of sand tufa endolithic microbial community, Mono Lake (California). Chemical Geology 217, 77–87. doi:10.1016/j.chemgeo.2004.12.004

Spencer, R., Baedecker, M.J., Eugster, H.P., Forester, R.M., Goldhaber, M.B., Jones, B.F., Kelts, K.,

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

McKenzie, J., Madsen, D.B., Rettig, S.L., Rubin, M., Bowser, C.J., 1984. Great Salt Lake, and precursors, Utah: The last 30,000 years. Contributions to Mineralogy and Petrology 86, 321–334.

Sturchio, N.C., 1990. Radium isotopes, alkaline earth diagenesis, and age determination of travertine from Mammoth Hot Springs, Wyoming, U.S.A. Applied Geochemistry 5, 631–640.

Suess, E., Balzer, W., Hesse, K.-F., Müller, P.-J., Ungerer, C.A., Wefer, G., 1982. Calcium carbonate hexahydrate from organic-rich sediments of the Antarctic Shelf: Precursors of glendonite. Science 216, 1128–1131. doi:10 .1126 /science .216 .4550 .1128.

Sugitani, K., Grey, K., Allwood, A., Nagaoka, T., Mimura, K., Minami, M., Marshall, C.P., Kranendonk, M.J. Van, Walter, M.R., 2007. Diverse microstructures from Archaean chert from the Mount Goldsworthy-Mount Grant area, Pilbara Craton, Western Australia: Microfossils, dubiofossils, or pseudofossils? Precambrian Research 158, 228–262. doi:10.1016/j.precamres.2007.03.006

Swart, P.K., 2015. The geochemistry of carbonate diagenesis: The past, present and future. Sedimentology 62, 1233–1304. doi:10.1111/sed.12205

Takashima, C., Kano, A., 2008. Microbial processes forming daily lamination in a stromatolitic travertine. Sedimentary Geology 208, 114–119. doi:10.1016/j.sedgeo.2008.06.001

Tanner, L.H., 2010. Continental Carbonates as Indicators of Paleoclimate. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds.), Carbonates in Continental Settings: Geochemistry, Diagenesis and Applications. Developments in Sedimentology 62. Elsevier, Amsterdam, pp. 179–214.

Tarutani, T., Clayton, R.N., Mayeda, T.K., 1969. The effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water. Geochimica et Cosmochimica Actachim. Acta 33, 987–996.

Thorrold, S.R., Campana, S.E., Jones, C.M., Swart, P.K., 1997. Factors determining δ^{13}C and δ^{18}O fractionation in aragonitic otoliths of marine fish. Geochimica et Cosmochimica Acta 61, 2909–2919.

Toker, E., Kayseri-Özer, M.S., Özkul, M., Kele, S., 2015. Depositional system and palaeoclimatic interpretations of Middle to Late Pleistocene travertines: Kocabas, Denizli, south-west Turkey. Sedimentology 1360–1383. doi:10.1111/sed.12186

Tosca, N., Masterson, A., 2014. Chemical controls on incipient Mg-silicate crystallisation at 25°C : implications for early and late diagenesis. Clay Minerals 49, 165–194.

Tosca, N.J., Macdonald, F.A., Strauss, J. V., Johnston, D.T., Knoll, A.H., 2011. Sedimentary talc in Neoproterozoic carbonate successions. Earth and Planetary Science Letters 306, 11–22. doi:10.1016/j.epsl.2011.03.041

Tucker, M., Wright, V.P., 1990. Carbonate sedimentology. Blackwell Scientific Publications.

Turner, E.C., Jones, B., 2005. Microscopic calcite dendrites in cold-water tufa: implications for nucleation of micrite and cement. Sedimentology 52, 1043–1066. doi:10.1111/j.1365-3091.2005.00741.x

Vasconcelos, C., McKenzie, J.A., 1997. Microbial mediation of modern dolomite precipitation and diagenesis under anoxic conditions (Lagoa Vermelha, Rio de Janeiro, Brazil). Journal of Sedimentary Research 67, 378–390.

Verrecchia, E.P., 2000. Fungi and Sediments. In: Riding, R., Awramik, S.M. (Eds.), Microbial Sediments. Springer Verlag, New York, pp. 68–75.

Verrecchia, E.P., Braissant, O., Cailleau, G., 2006. The oxalate-carbonate pathway in soil carbon storage: the role of fungi and oxalotrophic bacteria. In: Gadd, G.M. (Ed.), Fungi in the Biogeochemical Cycles. Cambridge University Press, UK, pp. 289–310.

Verrecchia, E.P., Dumont, J.-L., Verrecchia, K.E., 1993. Role of calcium oxalate biomineralization by

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

fungi in the formation of calcretes: A case study from Nazareth, Israel. Journal of Sedimentary Petrology 63, 1000–1006.

Verrecchia, E.P., Verrecchia, K.E., 1994. Needle-fiber calcite: a critical review and a proposed classification. Journal of Sedimentary Research A64, 650–664.

Veysey, J., Fouke, B.W., Kandianis, M.T., Schickel, T.J., Johnson, R.W., Goldenfeld, N., 2008. Reconstruction of Water Temperature, pH, and Flux of Ancient Hot Springs from Travertine Depositional Facies. Journal of Sedimentary Research 78, 69–76. doi:10.2110/jsr.2008.013

Visscher, P.T., Stolz, J.F., 2005. Microbial mats as bioreactors: Populations, processes and products. Palaeogeography, Palaeoclimatology, Palaeoecology 219, 87–100. doi:10.1016/j.palaeo.2004.10.016

Wacey, D., 2009. Early Life on Earth: A Practical Guide. Springer, Dordrecht.

Wacey, D., Gleeson, D., Kilburn, M.R., 2010. Microbialite taphonomy and biogenicity: New insights from NanoSIMS. Geobiology 8, 403–416. doi:10.1111/j.1472-4669.2010.00251.x

Wainer, K., Genty, D., Blamart, D., Daëron, M., Bar-Matthews, M., Vonhof, H., Dublyansky, Y., Pons-Branchu, E., Thomas, L., Calsteren, P. van, Quinif, Y., Caillon, N., 2011. Speleothem record of the last 180 ka in Villars cave (SW France): investigation of a large d18O shift between MIS6 and MIS5. Quaternary Science Reviews 30, 130–146.

Warren, J.K., 2016. Evaporites - A Geological Compendium, 2nd ed. Springer.

Wassenburg, J.A., Immenhauser, A., Richter, D.K., Jochum, K.P., Fietzke, J., Deininger, M., Goos, M., Scholz, D., Sabaoui, A., 2012. Climate and cave control on Pleistocene/Holocene calcite-to-aragonite transitions in speleothems from Morocco: Elemental and isotopic evidence. Geochimica et Cosmochimica Acta 92, 23–47. doi:10.1016/j.gca.2012.06.002

Watanabe, Y., Martini, J.E.J., Ohmoto, H., 2000. Geochemical evidence for terrestrial ecosystems 2.6

ACCEPTED MANUSCRIPT

billion years ago. Nature 408, 574–578. doi:10.1038/35046052

Watkins, J.M., Hunt, J.D., Ryerson, F.J., DePaolo, D.J., 2014. The influence of temperature, pH, and growth rate on the d18O composition of inorganically precipitated calcite. Earth and Planetary Science Letters 404, 332–343. doi:10.1016/j.epsl.2014.07.036

Westaway, R., 1993. Neogene evolution of the Denizli region of western Turkey. Journal of Structural Geology 15, 37–53. doi:10.1016/0191-8141(93)90077-N

White, R.M.P., Dennis, P.F., Atkinson, T.C., 1999. Experimental calibration and field investigation of the oxygen isotopic fractionation between biogenic aragonite and water. Rapid Commun. Mass Spectrom. 13, 1242–1247.

Whiticar, M.J., Suess, E., 1998. The cold carbonate connection between Mono Lake, California and the Brans¢eld Strait, Antarctica. Aquatic Geochemistry Geochem. 4, 429–454.

Woo, K.S., Choi, D.W., Lee, K.C., 2008. Silicification of cave corals from some lava tube caves in the Jeju Island, Korea: Implications for speleogenesis and a proxy for paleoenvironmental change during the Late Quaternary. Quaternary International 176–177, 82–95. doi:10.1016/j.quaint.2007.05.008

Wright, P., Tosca, N., 2016. A Geochemical Model for the Formation of the Pre-Salt Reservoirs , Santos Basin, Brazil : Implications for Understanding Reservoir Distribution. In: Search and Discovery Article. AAPG, p. 51304.

Wright, P.V., 2012. Lacustrine carbonates in rift settings: the interaction of volcanic and microbial processes on carbonate deposition. Geological Society of London, Special Publications 370(1), London, IK.

Wright, P.V., 1986. The role of fungal biomineralization in the formation of Early Carboniferous soil fabrics. Sedimentology 33, 831–838.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Wright, V.P., Alonso-Zarza, A.M., Sanz, M.E., Calvo, J.P., 1997. Diagenesis of Late Miocene micritic lacustrine carbonates, Madrid Basin, Spain. Sedimentary Geology 114, 81–95. doi:10.1016/S0037-0738(97)00059-6

Wright, V.P.P., Barnett, A.J.A.J., 2015. An abiotic model for the development of textures in some South Atlantic early Cretaceous lacustrine carbonates. In: Bosence, D.W.J., Gibbons, K.A., Heron, D.P. Le, Morgan, W.Q., Pritchard, T., Vining, B.A. (Eds.), Microbial Carbonates in Space and Time: Implications for Global Exploration and Production. Geological Society of London, Special Publications, London, UK, pp. 209–219. doi:http://dx.doi.org/10.1144/SP418.3

Yan, H., Schmitt, A.D., Liu, Z., Gangloff, S., Sun, H., Chen, J., Chabaux, F., 2016. Calcium isotopic fractionation during travertine deposition under different hydrodynamic conditions: Examples from Baishuitai (Yunnan, SW China). Chemical Geology 426, 60–70. doi:10.1016/j.chemgeo.2016.02.002

Yoreo, J.J. De, Gilbert, P.U.P.A., Sommerdijk, N.A.J.M., Penn, R.L., Whitelam, S., Joester, D., Zhang, H., Rimer, J.D., Navrotsky, A., Banfield, J.F., Wallace, A.F., Michel, F.M., Meldrum, F.C., Colfen, H., Dove, P.M., 2015. Crystallization by particle attachment in synthetic, biogenic, and geologic environments. Science 349, aaa6760-1-9. doi:10.1126/science.aaa6760

Zamanian, K., Pustovoytov, K., Kuzyakov, Y., 2016. Pedogenic carbonates: Forms and formation processes. Earth-Science Reviews 157, 1–17. doi:10.1016/j.earscirev.2016.03.003

Zamarreño, I., Anadón, P., Utrilla, R., 1997. Sedimentology and isotopic composition of Upper Palaeocene to Eocene non-marine stromatolites, eastern Ebro Basin, NE Spain. Sedimentology 44, 159–176. doi:10.1111/j.1365-3091.1997.tb00430.x

Zeebe, R.E., Wolf-Gladrow, D.A., 2001. CO_2 in seawater: equilibrium, kinetics, isotopes, 1st ed, Elsevier Oceanography Series. Elsevier Science. doi:10.1016/S0924-7963(02)00179-3

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Zeyen, N., Benzerara, K., Li, J., Groleau, A., Balan, E., Robert, J.-L., Estève, I., Tavera, R., Moreira, D., López-García, P., 2015. Formation of low-T hydrated silicates in modern microbialites from Mexico and implications for microbial fossilization. Frontiers in Earth Science 3, 1–23. doi:10.3389/feart.2015.00064

Zhang, H., Cai, Y., Tan, L., Qin, S., An, Z., 2014. Stable isotope composition alteration produced by the aragonite-to-calcite transformation in speleothems and implications for paleoclimate reconstructions. Sedimentary Geology 309, 1–14. doi:10.1016/j.sedgeo.2014.05.007

Zhang, Z., Xie, Y., Xu, X., Pan, H., Tang, R., 2012. Transformation of amorphous calcium carbonate into aragonite. Journal of Crystal Growth 343, 62–67. doi:10.1016/j.jcrysgro.2012.01.025

Zhou, G.-T., Zheng, Y.-F., 2001. Chemical synthesis of $CaCO_3$ minerals at low temperatures and implication for mechanism of polymorphic transition. N. Jb. Miner. Abh 176, 323–343.

Zhu, T., Dittrich, M., 2016. Carbonate Precipitation through Microbial Activities in Natural Environment, and Their Potential in Biotechnology: A Review. Frontiers in bioengineering and biotechnology 4, 1–21. doi:10.3389/fbioe.2016.00004

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

Figure and Table captions

Figure 1: Schematic drawing and cross-section of the location and transitions between different non-marine depositional environments and their deposits (based on Freytet and Plaziat, 1982; Arp, 1995; Pedley and Rogerson, 2010; Brasier, 2011; Wright, 2012; Della Porta, 2015) considered in this review. The extent of the reference examples of Table 1 is indicated below the cross-section.

Figure 2: Schematic drawing and cross-section showing fluids involved in formation and early diagenesis of non-marine carbonates. Early diagenesis may take place from marine influenced, evaporative fluids over freshwater and fluids that have migrated up from the deep(er) subsurface at, for example hot springs.

Figure 3: Precipitation and early diagenesis in the micro-environment. (A) Porous aggregates of straight monocrystalline Needle Fibre Calcite (NFC) crystals from a moonmilk speleothem of Koselevka cave, Slovenia. SEM image, secondary electrons mode (Image: courtesy of Dr. A. Martín-Pérez; Martín-Pérez and Košir, 2017). (B) Bundles of aragonite needles radiating outward from a degraded *Aquificales* filament at the transition between the Apron-Channel and Pond Facies at New Grassy Spring (Fouke, 2011) (Mammoth Hot Springs, Yellowstone National Park, USA). SEM image, secondary electron mode. (C) Detail of B showing mineralized extracellular polymeric substances (EPS) with honeycomb structure between the aragonite needles. (Sample taken and provided by L. DeMott). (D) SEM image, secondary electron mode, of a polished thin section showing the contact between a matrix made of Mg-silicate (Mg-si) filaments and aragonite (Ar) fibre fans that seem to nucleate from this clay matrix. Mg-silicates are closely linked and interfingering with fibrous aragonite in crusts formed at the transition from marine to hypersaline conditions in the Danakil Depression (Afar, Ethiopia). Crusts occur after two incursions by the Red Sea during the Pleistocene (MIS7 and MIS5e). Although similar crusts were formed, Mg-silicates are only found in the younger of the two marine to hypersaline sequences (MIS 5e). With less than 100 kyr difference in age, all Mg-

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silicates have been dissolved and the majority of the aragonite has been replaced by calcite in the older sequence. (Image: courtesy of Dr. D. Jaramillo-Vogel; Jaramillo-Vogel et al., 2016).

Figure 4: Neomorphism. (A) Calcite rhomb crystals, consisting of different platelets, are encasing and growing outward from aragonite needles in an encrusted filamentous mat sample at the transition between the Apron-Channel and Pond Facies (Fouke, 2011) of the active New Grassy Spring at Mammoth Hot Springs (Yellowstone National Park, USA). SEM image, secondary electrons mode. (Sample taken and provided by L. DeMott). (B) Transmitted light image of a large, anhedral, equant calcite mosaic. The primary fibrous fabric of bundles of aragonite crystals became neomorphosed and gives the calcite crystals a brownish, inclusion-rich appearance. The aragonite needles seem to have been forming elongated textures that nucleated and grew from different, still faintly recognizable primary horizons (red arrows). Small-scale dissolution is indicated by black arrows. (Y-10 core, Mammoth Hot Springs, Yellowstone National Park, USA). (C) Image with crossed polars of (B) better showing the fibrous texture of the primary aragonite. (D) Neomorphic, larger radial fibrous calcite crystals build from an earlier radial fibrous calcite phase that nucleated from clotted micrite thereby obliterating the previous clotted texture (Great Salt Lake, USA). Transmitted light with crossed polars of stained thin section (Image: courtesy of Dr. P. Homewood and Dr. M. Mettraux, ongoing study).

Figure 5: Cements and (spar)micritisation. (A) Transmitted light image with crossed polars of micritic-sparitic layered, pendant cements lining the upper side of a cavity (Great Salt Lake, USA) (Courtesy of Dr. P. Homewood and Dr. M. Mettraux). (B) Platy calcite rhombs forming pyramidal to bipyramidal composite crystals, cementing framework porosity around moss branches in Pleistocene travertine deposits (Cakmak quarry, Denizli Basin, Turkey). SEM image, secondary electron mode. (C) Isopacheous, transparent calcite cement (red arrow) around microporous, micritic dendrite textures (Cakmak quarry, Denizli Basin, Turkey). Transmitted light. (D) Calcitic, acicular cement growing inside primary porosity of Great Salt Lake microbialites along the northeastern side of Stansbury Island.

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Transmitted light image (Image: courtesy of Dr. M. Vanden Berg; Chidsey et al., 2015). (E) Neomorphosed aragonite needles leaving a microporous fabric are surrounded and encased by a subhedral, equant calcite cement in Pleistocene travertine deposits (Gardiner area, USA). SEM image, secondary electron mode.(F) Transmitted light image of microbial laminites made of single or multiple micritic, organic films curled and folded to form open interlamina cavities lined by calcite cement. The subhedral calcite crystals are interpreted as a geodic cement resulting from the evaporation of water retained in the microbial mat. The folds apparently derive from diapiric deformation (Oliviera Quarry, Rapolano, Siena, Italy) (Image: courtesy of Prof. A. Gandin; Gandin and Capezzuoli, 2014). (G) Repetitive events of sparmicritisation (red arrows) of botryoidal growth radial fibrous calcite increments (Great Salt Lake, USA). Transmitted light (Image: courtesy of Dr. P. Homewood and Dr. M. Mettraux). (H) Transmitted light image of stained thin section showing possible fungal threads affecting microbialite clasts or "bedrock" (Great Salt Lake, USA) (Image: courtesy of Dr. P. Homewood and Dr. M. Mettraux, ongoing study).

Figure 6: Replacement processes. (A) Transmitted light image of calcite pseudomorphs after ikaite (Ik; large, clear nicely shaped crystals) leaving a porous fabric behind (blue resin is pore space) (north shore of Mono Lake, USA). (B) and (C) Transmitted light and cathodoluminescence image of extensively silicified dolomite (D, bright, orange-yellow luminescent). Different silica generations represent authigenic quartz (Qz, non luminescent) followed by thinly laminated chalcedony (Cad, brownish to non luminescent). Relict dolomite represent dolomitized stromatolites deposited in hypersaline lacustrine settings (Aptian, Angola; Foubert et al., 2014). (D) Spheroidal dolomite crystals with fibrous-radial texture and concentric bands cement and replace aragonite crystals (stained red) in a crust speleothem of Snežna Jama, Slovenia (Martín-Pérez et al., 2015b) (Image: courtesy of Dr. A. Martín-Pérez).

Figure 7: Weathering processes. (A) Dissolution cavities and vugs with clayey infill in Pleistocene Distal Slope travertine (encrusted gas bubbles, fossilized microbial and algal mats) (Gardiner area,

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USA). (B) Large dissolution cavity showing, cemented angular travertine clasts (arrows) resulting of collapse breccia, overlain again by travertine deposits (Proximal Slope Facies in Gardiner area, USA). (C) Cold cathodoluminescence image of neomorphosed and cemented, layered travertine (Holocene, Mammoth Hot Springs, Yellowstone National Park, USA). Dull, orange and non-luminescent laminae are alternating in the calcite cement crystals and show, at several levels (arrows) evidence of dissolution phases. (D) Water filled, small, rimmed pool at an active spring (Edipsos, Greece). The green-brownish color links to microorganisms living in the pool and enclosing coated gas bubbles (arrows). Scale is in centimeters. (E) View of (D) when the pool becomes temporarily dry (days-week) and dessication starts. Mineralized filaments (arrows) bind the small, coated gas towers that close and shrink upon drying out (Edipsos, Greece). Scale is in centimeters. (F) Soil nodules showing (circumgranular) cracks (Great Salt Lake, USA). (Image: courtesy of Dr. P. Homewood and Dr. M. Mettraux, ongoing study).

Figure 8: Compilation of $\delta^{13}C$ and $\delta^{18}O$ values in non-marine carbonate case studies (see Table 1) showing the great variation in stable isotopic signatures. Isotopic signatures of common water and carbon sources in the non-marine environment are outlined (grey arrows), as well as the influence of common precipitation (grey) and diagenetic (red arrows) processes (Hoefs, 2004; Pentecost, 2005; Moore and Wade, 2013). Inverted J-trend classically reported for diagenesis (of marine rocks) by freshwater, charged with soil CO_2 (Lohmann, 1988). The covariance of $\delta^{13}C$ and $\delta^{18}O$ in many non-marine carbonates relates to simultaneous processes of CO_2 degassing, evaporation and cooling of the fluid (Pentecost, 1995; Fouke et al., 2000; Arp et al., 2013b; Della Porta, 2015). For Edipsos hot springs (Greece) and Mammoth Hot Springs (Holocene): personal data; for (sub)tropical soils: no $\delta^{18}O$ available for calcite; GSL = Great Salt Lake.

Figure 9: Primary fabrics? (A)-(B) 3D reconstructed volume, based on micro-computer tomography (µCT) of a Proximal Slope sample from an inactive spring (Skyscan 2211, 9.2 µm resolution). Alternating laminae of aragonitic shrubs, growing perpendicular to the slope, and aragonite-

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encrusted *Aquificales* filaments, typical of the Apron-Channel Facies (Fouke, 2011), that tend to 'hang down' the slope. Sample comes from a fossil location equivalent to the one indicated by the white square in B (Mammoth Hot Springs, Yellowstone National Park, USA). The filamentous *Aquificales* prefer temperatures between 65°C and 71°C, close to the vent. When flow increases and the high temperature window shifts downstream, they can prograde over the top of the slope. When flow decreases, they retreat and shrubs form on the slope and slope break. This creates some primary flow-driven, 'cross lamination' in a travertine crust. (C)-(D) Well-laminated carbonate crust with Fe-oxide rich laminations that formed in an active spring at the rim of a small channel within 0.5 m distance of the vent (Edipsos, Greece). The laminations cap an initial topography and smoothen it.

Figure 10: A pyramidal, process-centered framework for understanding and addressing non-marine (early) carbonate diagenesis. For full explanation, the reader is referred to the text. A number of fabrics discussed in the text and related to the different 'end-member' diagenetic processes, marking the corners of the frontal triangle, are schematically illustrated.

Figure 11: Micro-computed tomography (µCT) to study 3D properties of diagenetically altered fabrics. (A) Color labeled pore space in Pleistocene spring carbonate pervasively cemented by an isopachous calcite rim (Cakmak quarry, Denizli Basin, Turkey). Each color marks a separate pore space, not connected to the others. (B) Illustration of the 3D distribution of rod (blue) and cube (green) shaped pores (Claes et al., 2016) in the same sample. Pore bodies were split using a watershed algorithm. (Nanotom high-resolution X-ray µCT, 4 µm resolution)

Table 1: A selection of reference case studies for each non-marine depositional environment with overview of their depositional, hydrogeochemical and (paleo)environmental characteristics that are often referred to and used in this review. They have, in general, never been buried and (early) diagenetic processes have been carefully addressed in literature or are under investigation.

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Table 2**:** Range of rates of early diagenesis (chiefly neomorphism and cementation processes) as found in literature.

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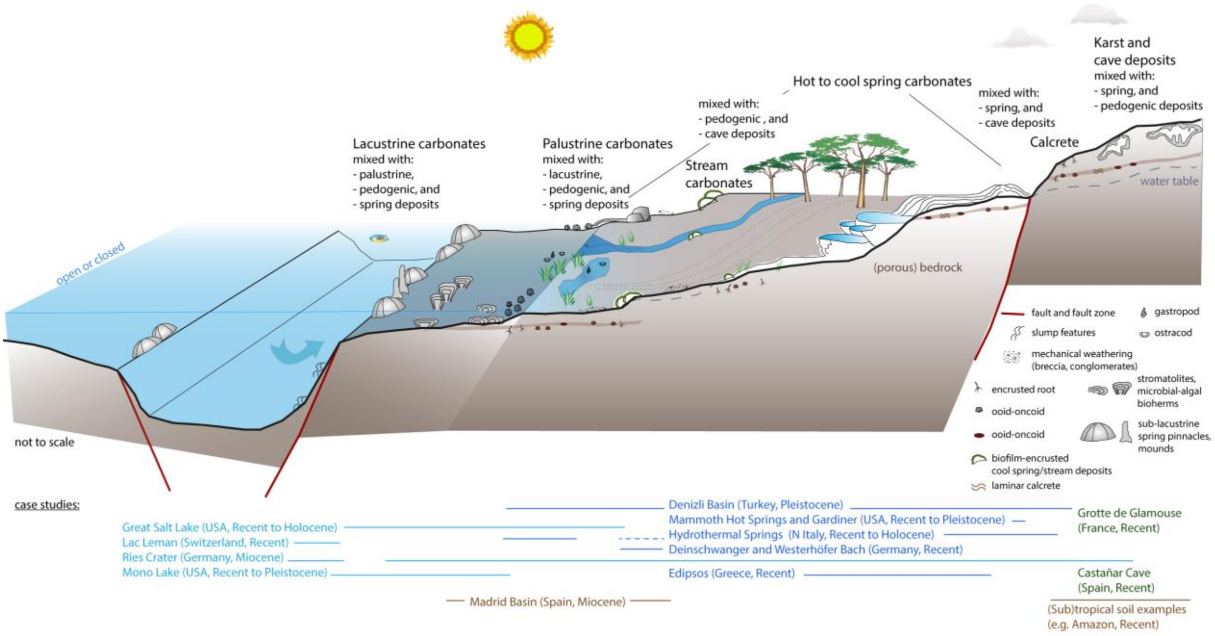

Figure 1

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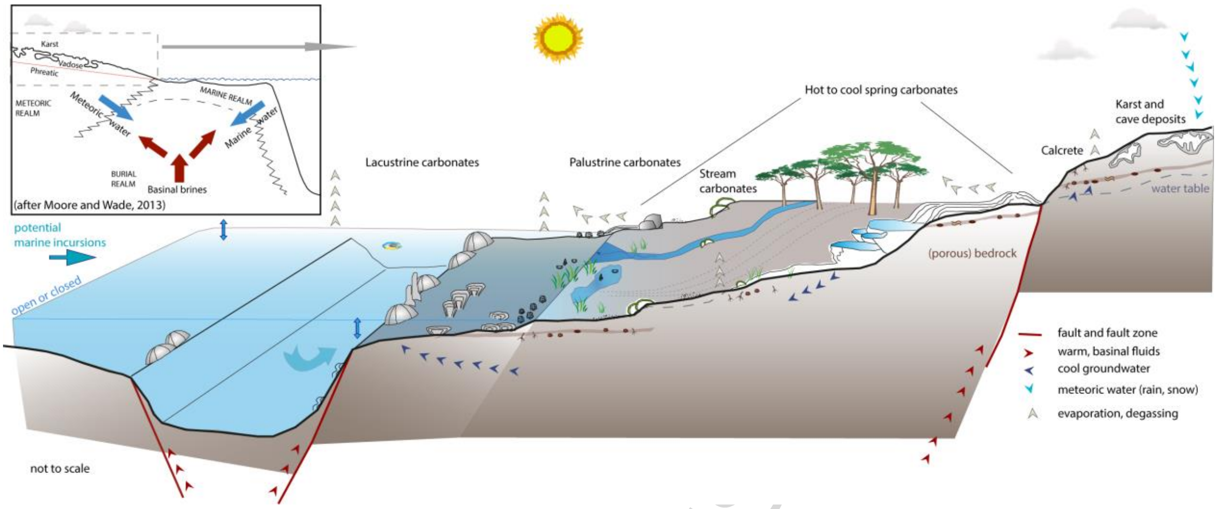

Figure 2

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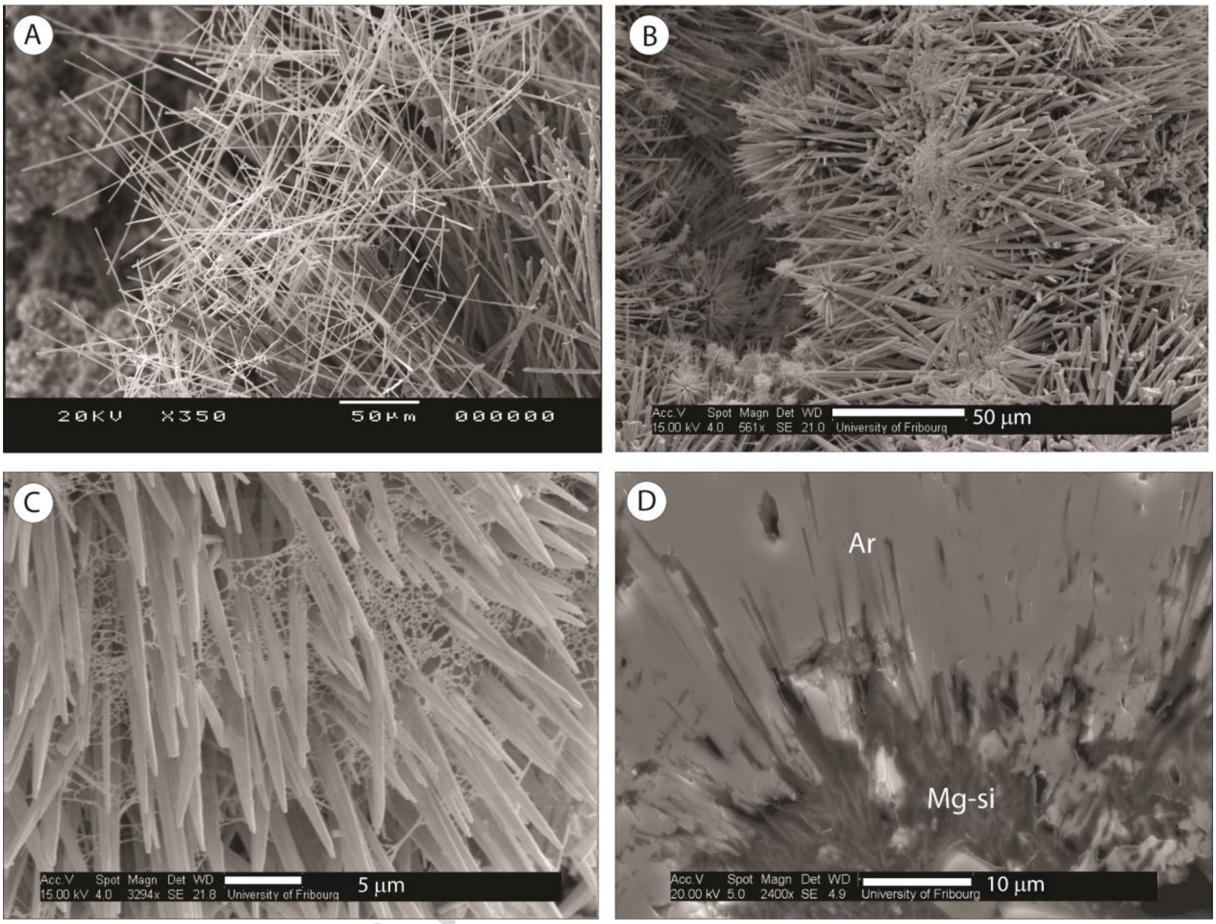

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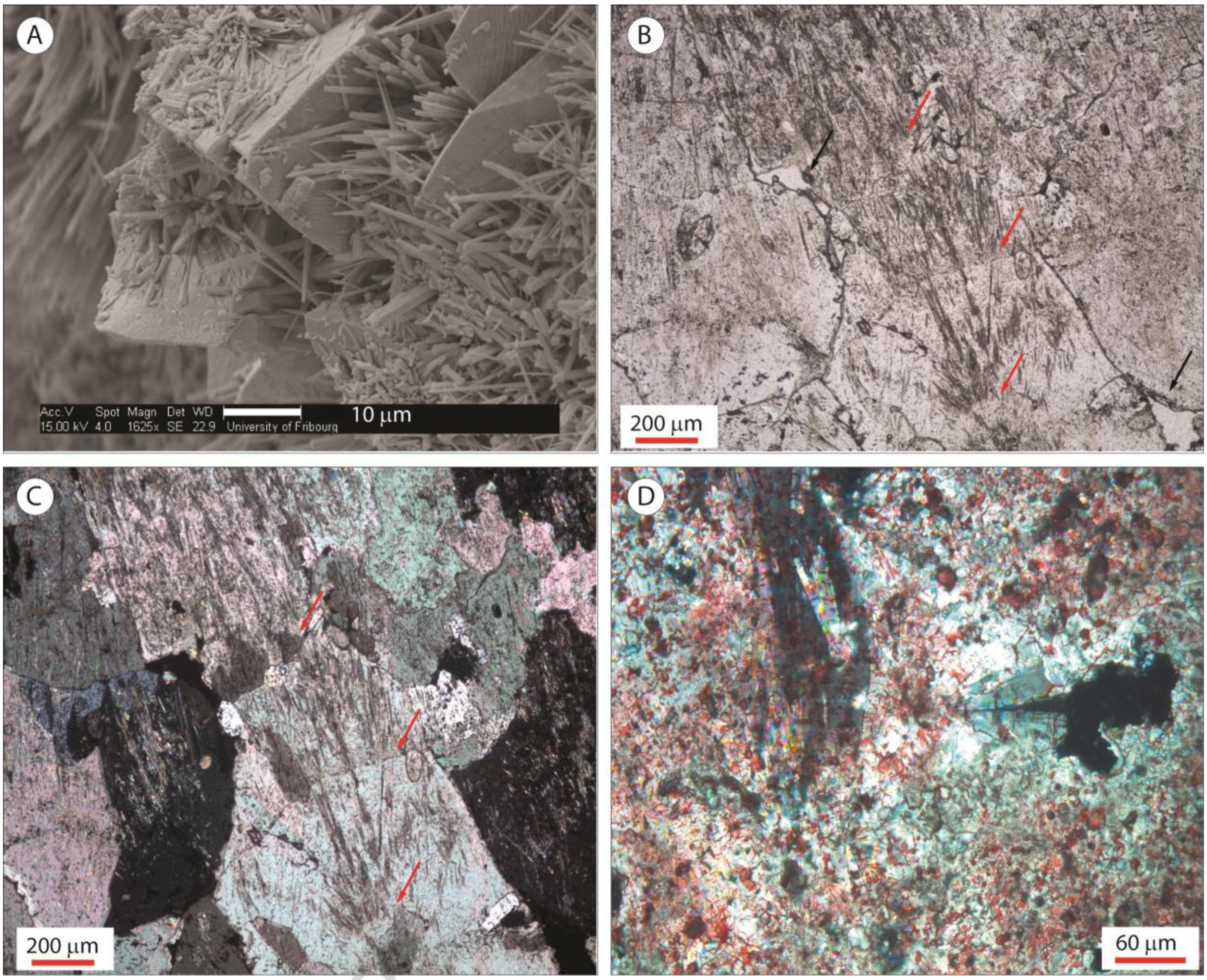

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Figure 4

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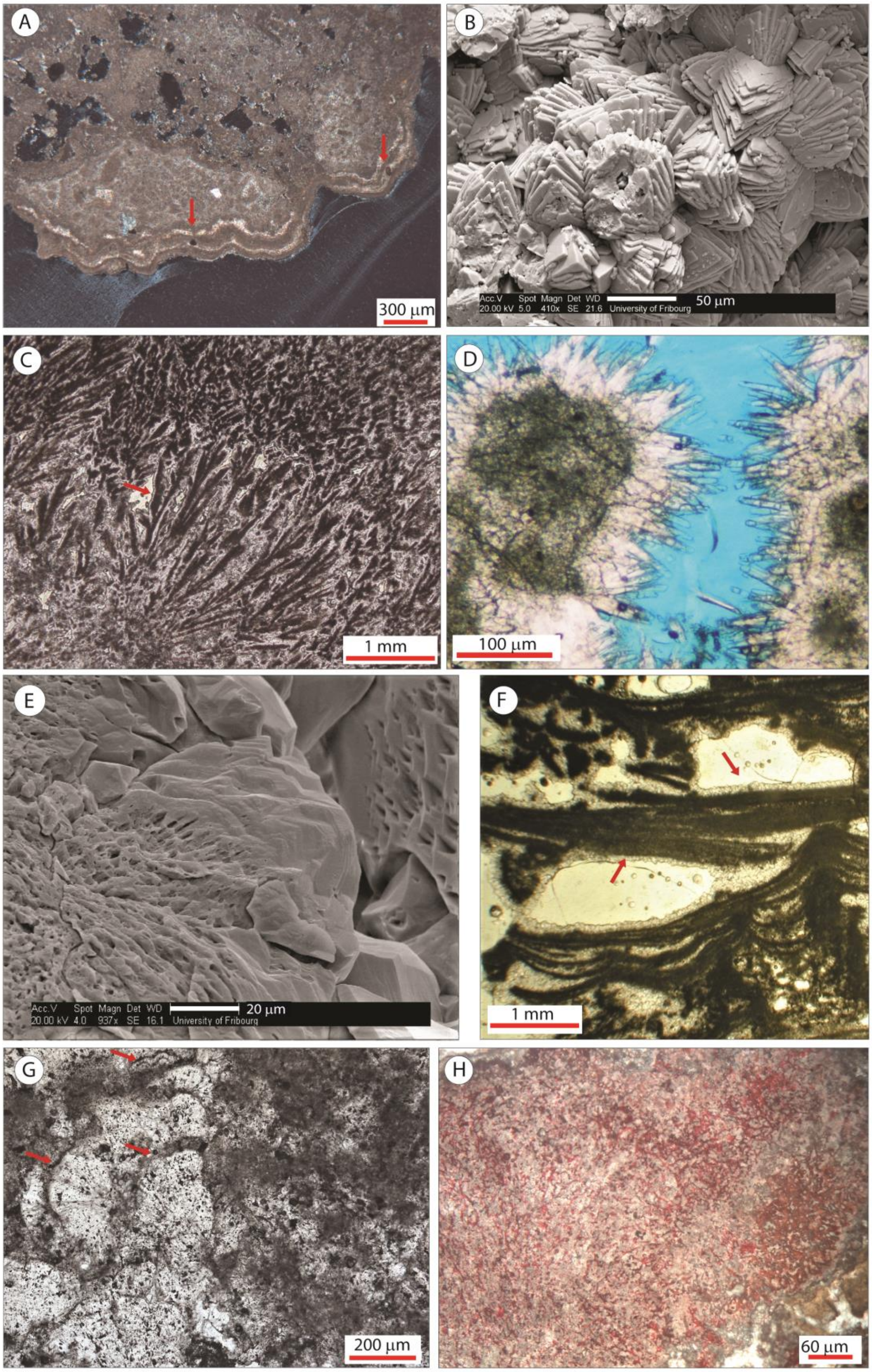

Figure 5

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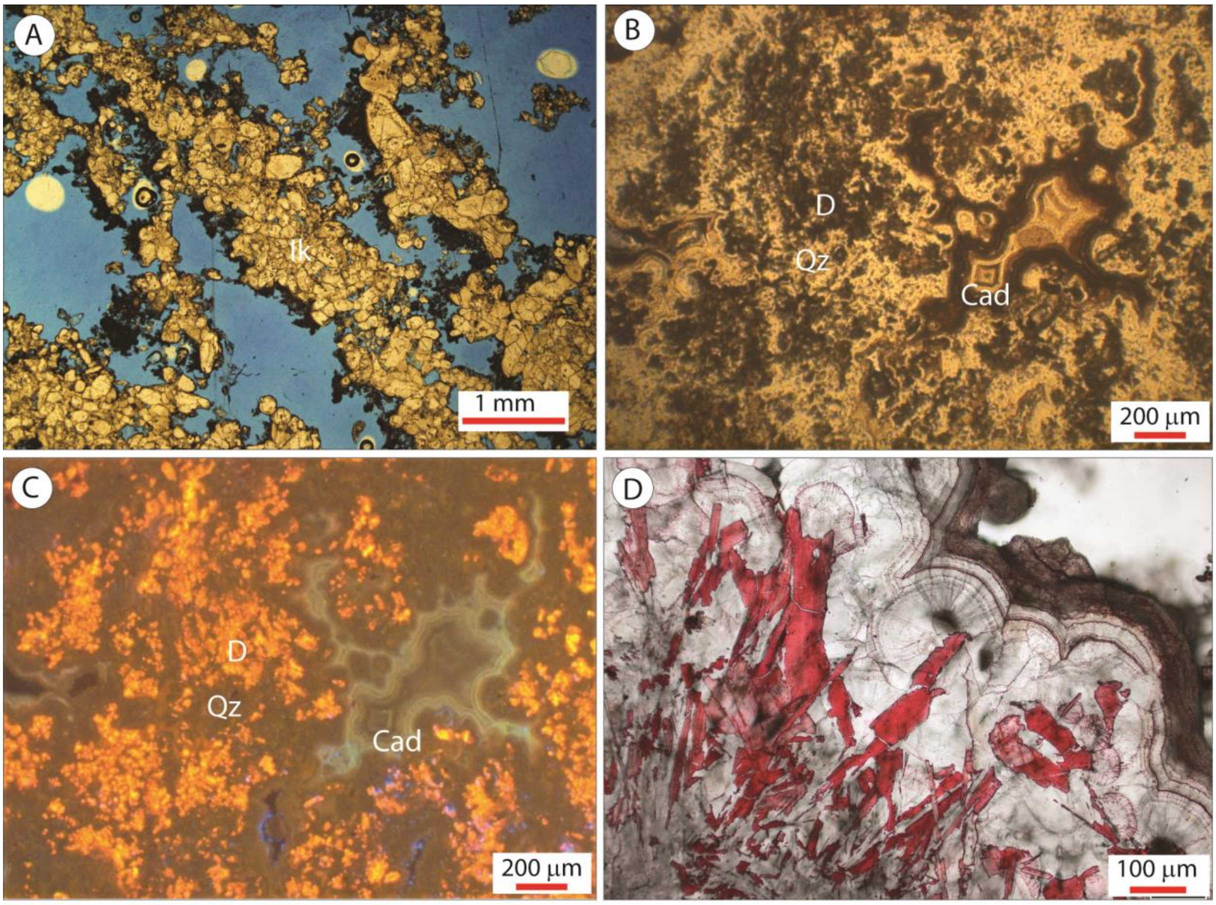

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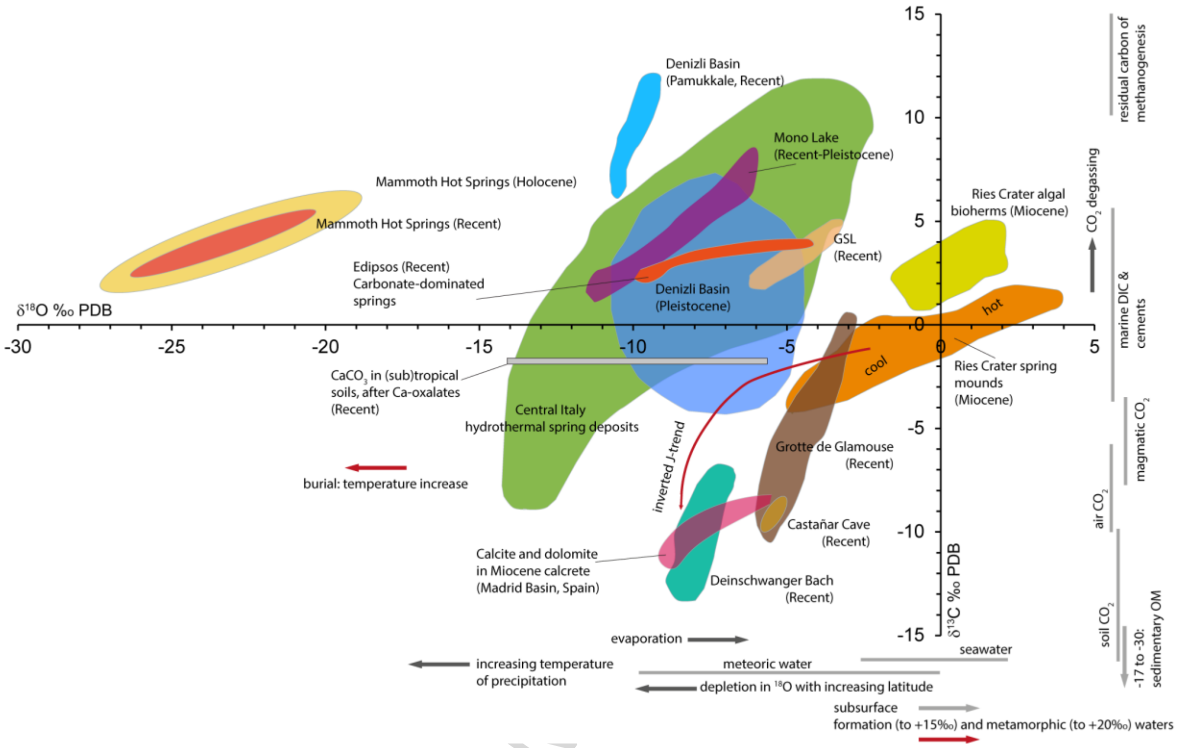

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Figure 8

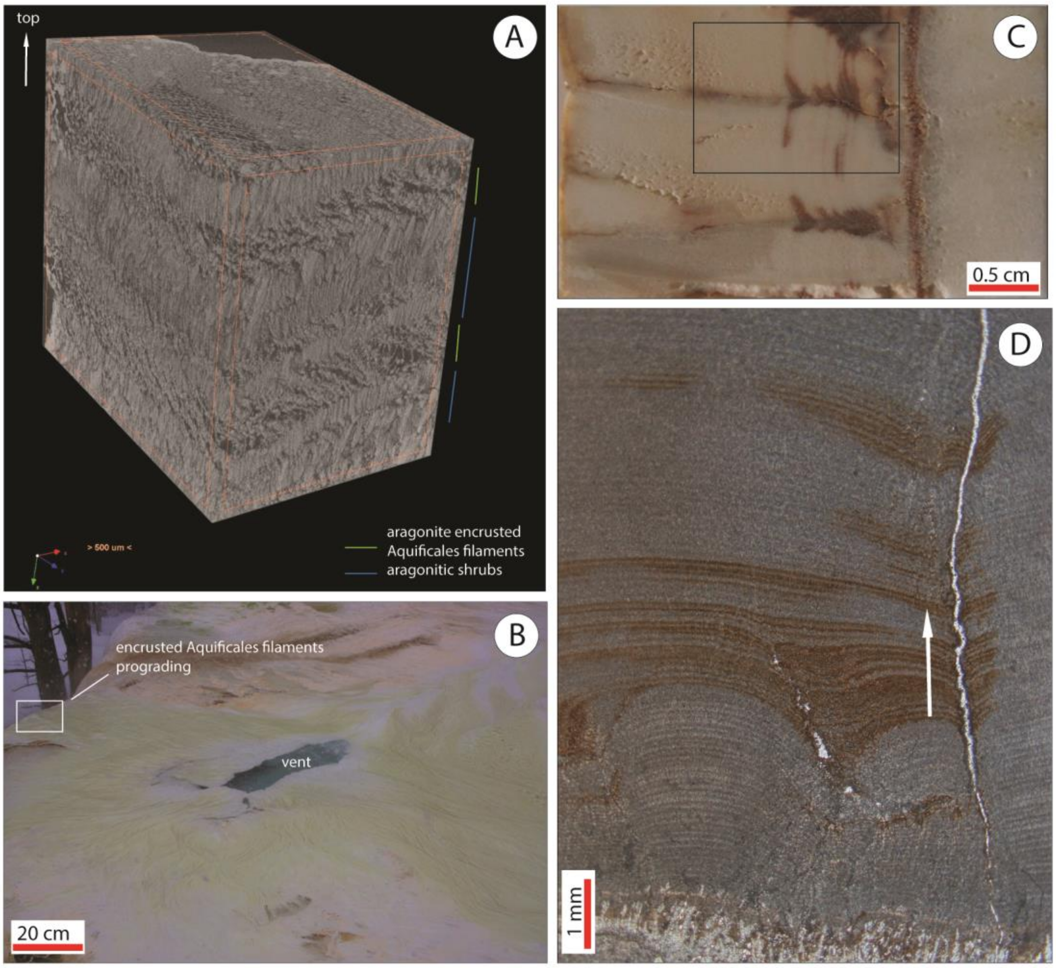

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Figure 9

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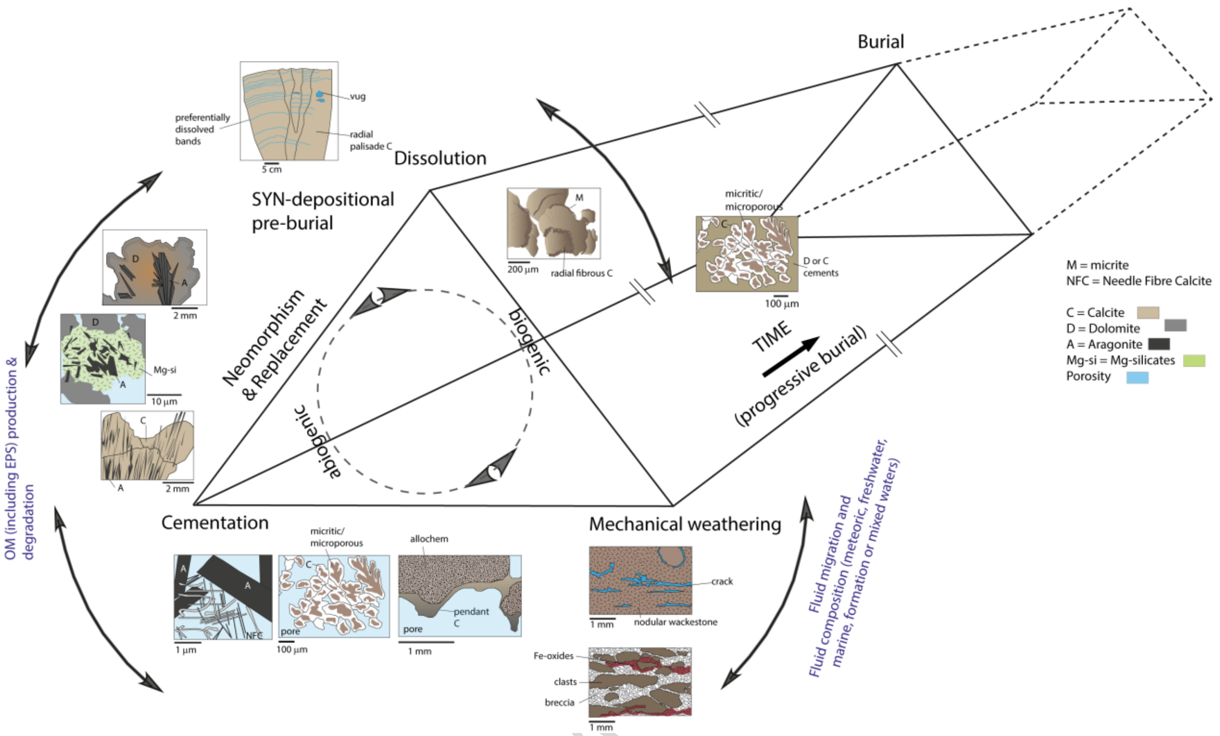

Figure 10

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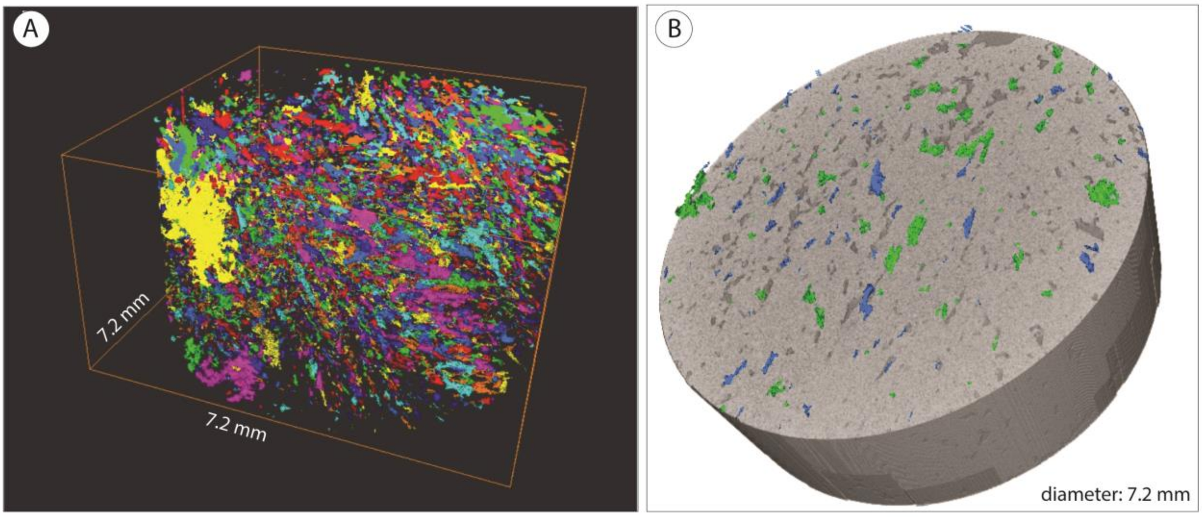

Figure 11

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Non-marine carbonate environment	*Description of setting, water chemistry and depositional facies*	*Early diagenetic processes described*	*References*
Marginal lacustrine and palustrine			
Lac Leman (Geneva, Switzerland)	Recent monomictic, mesotrophic lake (T: 5-20°C; Mg/Ca: 0.20 - 0.26). Climate: Moderate. Algal blooms occur twice a year in May and July. . SW part (Geneva Bay) is well-oxygenated and mixed due to episodic strong wind and wave action. Deposits: low-magnesium calcite ooid and oncoid deposits containing scattered (filamentous) algal and shell fragments (charophytes, gastropods, and pelecypods). Laminated lacustrine marls and chalk and glaciolacustrine silty clay.	Organic matter degradation, aggrading neomorphism	(Davaud and Girardclos, 2001; Plee, 2008; Martignier et al., 2017)
Great Salt Lake (Utah, USA)	Recent to Holocene, endorheic polymictic and stratified hypersaline lake in normal fault-bounded graben (T: <0 - 35°C; pH: 7.6 - 8.4; salinity: 12 - 27%; Mg/Ca: 9-115; Alkalinity: 5.4 - 8.4 meq/L). Evaporative remnant of Pleistocene Lake Bonneville. Climate: semi-arid, precipitation: 125 - 375 mm/y. Deposits: Calcite, aragonite and dolomite. Ooidal sands, bioherms parallel to shoreline, microbialites (including stromatolites) along current lake side, ridges with spring mounds above the current lake shore, evaporates in salt flat.	Replacement, cementation; mechanical weathering, dissolution	(Eardley, 1938; Sandberg, 1975; Currey and James, 1982; Spencer et al., 1984; Currey and Oviatt, 1985; Pedone and Dickson, 2000; Chidsey et al., 2015; Bouton et al., 2016a, 2016b; Pace et al., 2016; Lindsay et al., 2017)
Ries Crater lake (South Germany)	Circular depression resulting from a meteoric impact (initial diameter 10 km) filled with Miocene lacustrine and submerged spring carbonates at the rim. Water chemistry: evolution of a highly alkaline, stratified soda lake (Na-Mg-CO_3-SO_4) to mesosaline lake (Na-Mg-Cl-SO_4) with occasional low salinity episodes during lake high stand and high-salinity conditions prevailing at the crater rim. Climate: semi-arid to arid. Deposits: supralitoral carbonate swamps and pedogenic carbonates, spring mounds, eulitoral coated grains, microbialites (including stromatolites) and algal bioherms, speleothems	Dissolution, micritisation, shrinkage, neomorphism, replacement, cementation	(Riding, 1979; Arp, 1995; Pache et al., 2001; Arp et al., 2013, 2017)
Mono Lake (CA, USA)	Pleistocene to Recent, endorheic alkaline lake located in an extensional, active volcanic basin near the Sierra Nevada (T: 1.5 - 23°C; pH: 9.7 - 10; salinity: > 90%; Alkalinity: 600 - 700 meq/l; Mg/Ca: 14). Climate: Mediterranean continental to subarctic. Precipitation mostly as snow (1600 mm/y). Deposits: Aragonite, Calcite and Ikaite precipitates (+assecory minerals) forming mounds or 'tufa pinnacles' where spring waters mix with the alkaline lake waters. Mg-silica formation within decaying endolithic cyanobacterial tufa sand communities.	Replacement (ikaite to calcite), organic matter degradation and Mg-silicate formation	(Shearman et al., 1989; Bischoff et al., 1993; Council and Bennett, 1993; Whiticar and Suess, 1998; Souza-Egipsy et al., 2005; Della Porta, 2015)
Pedogenic calcrete and palustrine			
(Sub)tropical soils (Bolivia, Ivory coast, Cameroon)	Amazon, Bolivia: Recent soils developed in Cretaceous to early Cenozoic sandstone formations (pH: 4.3 - 6.0). Climate: tropical wet and dry or savannah type to tropical rainforest type (>550m altitude). 1300-1600 mm/y rain. Deposits: Ca-oxalates near photosynthesizing tree *C. speciose* as byproduct in initial, carbonate free soils. Ivory Coast: Semidecidous, gallery forest. Climate: 1300-1500 mm/y rain, mean annual temperature: 24.5°C. Cameroon: Gallery forest. Climate: 1800 mm/y rain, mean annual temperature: 23 °C. Deposits: Ca-oxalates and $CaCO_3$ (euhedral calcitic rhombohedron, micritic aggregates, calcite pseudomorphoses on cellulose fibers, and parenchyma cells) in the iroko tree.	Replacement (oxalate-carbonate pathway, OCP), dissolution	(Bindschedler et al., 2010; Cailleau et al., 2011, 2014)
Madrid Basin (Spain)	Miocene alluvial, palustrine and lacustrine carbonate deposits with calcretes and dolocretes. Deposits: Micritic-microsparitic calcite (mudstones), siltstones and sepiolite (hydrated Mg-siliciate) with smaller amounts of illite, palygorskite and smectite formed in alluvial fans, channels, ponds and shallow lakes. Opaline chert, calcite and dolomite nodules and lenticular levels, calcified root mats, alveolar structures, fenestrae, silicified bioturbations in palustrine and pedogenic horizons.	Silicification, dolomitisation, dissolution, cementation, shrinkage cracks	(Armenteros et al., 1995; Calvo et al., 1995, 1999; Bustillo et al., 2002; Alonso-Zarza, 2003; Bustillo and Alonso-Zarza, 2007; Bustillo, 2010)
Caves			
Glamouse Cave (SE France)	Recent cave in dolomites and dolomitic limestones of Early Jurassic age. Climate: subhumid Mediterranean, with strong seasonality (annual precipitation: 791 mm; mean annual temperature: 14.1°C). Evaporation dominates from June until early September. Mediterranean C3 vegetation. Cave	Neomorphism, local dissolution related to organic matter decomposition	(Frisia, 1996; Frisia et al., 2002)

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	chemistry: humidity: 98-99%; temperature air: 14.5°C; pH: 7.65 - 7.85; pCO$_2$: 2.32 - 2.42; Mg/Ca: 1.39 - 0.31; Alkalinity: 178 – 281 mg/L; δ^{18}O$_{H2O}$: -5.9 to -6.5‰ SMOW. Deposits: stalagmites and flowstones of aragonite and calcite mineralogy		
Castañar cave (Spain)	Recent caves developed in dolomitic beds of Neoproterozoic rocks (Ibor anticline). Water chemistry: Mg/Ca: 0.5 – 1; mean annual air temperature 17°C; 100% humidity. Deposits: Frostworks, helictites, stalactites, stalagmites, draperies and flowstones. Mixed aragonite-calcite with minor dolomite-huntite-hydromagnesite and magnesite (in moonmilk and crusts).	Neomorphism, micritisation, corrosion, replacement (dolomitisation)	(Alonso-Zarza and Martín-Pérez, 2008; Martín-García et al., 2009, 2011, Martín-Pérez et al., 2012, 2015)
Spring and streams			
Denizli graben (SW Turkey)	Pleistocene spring carbonate mound and lacustrine deposits along extenstional and transtensional graben faults. Recent spring water composition at Pamukkale: Ca-Mg-SO$_4$-HCO$_3$-type, 35-57 °C (vent) - 20°C downstream, pH: 6.0 - 7.8. Deposits: spring mounds (up to 40 m high-200 m wide) exposed in quarries. Fissure ridges are common. Mounds are underlain by a subhorizontal facies, interpreted as wide, waterlogged flats and interlain with fluvial deposits.	Cementation, neomorphism (?), dissolution	(Lopez et al., n.d.; Westaway, 1993; Pentecost et al., 1997; Kele et al., 2011; De Filippis et al., 2012; Özkul et al., 2013; Van Noten et al., 2013; Lebatard et al., 2014; Claes et al., 2015, 2017; De Boever et al., 2017)
Mammoth Hot Springs and Gardiner quarries (Yellowstone National Park, USA)	Recent to Holocene hot spring deposits, within the active hydrothermal area of Yellowstone National Park. Located in the NS-aligned and faulted Norris-Mammoth Corridor. Water chemistry: Ca-Na-HCO$_3$-SO$_4$ -type, 73-25°C, pH: 6-8, Mg/Ca < 0.01 (Vent to Distal Slope), carbonate precipitation rates: 0.1-5 mm/day. Climate: subarctic/cold semi-arid. Deposits: Aragonite and calcite deposits forming mounds, terraces, fissure ridges showing a five-fold facies sequence from Vent to Distal Slope. 90% partitioning in phylogenetic diversity observed between the microbial communities inhabiting each facies. Filamentous *Aquificales* species dominant in near-vent environment. Pleistocene spring deposits exposed in (abandoned) Gardiner quarries and along road cuts. Travertine deposits in close spatial association with basalt columns, and interlain with glacial diamictite sediments. Similar five-fold facies sequence is recognizable in these deposits.	Neomorphism, cementation, shrinkage cracks, erosion, dissolution (including vugs to karst), brecciation and fracturing	(Sorey and Colvard, 1997; Fouke et al., 2000, 2003; Kharaka et al., 2000; Chafetz and Guidry, 2003; Kandianis et al., 2008; Veysey et al., 2008; Fouke, 2011; De Boever et al., 2017)
Thermal springs in northern Italy (Rome to Siena, Italy)	Present-day to Pleistocene, hydrothermal spring carbonates. Chiefly fault-controlled fluid pathways within Neogene extensional-transtensional Apennine back-arc collapse basin. Cooling magmatic intrusions present in subsurface. Regional Mesozoic limestone aquifer, interaction with Triassic evaporates. Water chemistry of active springs (strongly variable depending on subsurface pathways): Ca-HCO$_3$-SO$_4$ -type, pH: 6.0 - 7.15; Temperature: 17.1 - 65°C, pCO$_2$: -1.83 - 0.82; Mg/Ca: 0.3-0.5, δ^{18}O$_{H2O}$: -6.7 to -10.6‰ SMOW. Climate: Humid subtropical and oceanic (today). Deposits: Forming isolated masses up to 40-50 m thick and 5 km^2. Calcitic (and locally recent aragonitic) terraced and smooth slope, fissure ridge, reed mound, waterfall facies and shallow pools, ponds, breccia.	Cementation, neomorphism, sparmicritisation, shrinkage, dissolution, mechanical weathering (slope instability)	(Cipriani et al., 1977; Barazzuoli et al., 1988; Guo and Riding, 1992, 1994, 1998, 1999; Pentecost, 1995; Minissale et al., 2002; Brogi et al., 2007; Brogi and Capezzuoli, 2008; Pedley, 2009; Gandin and Capezzuoli, 2014; Della Porta et al., 2017)
Deinschwanger and Westerhöfer Bach (Germany)	Recent, cool spring and stream deposits in a karstic area. Water chemistry: Deinschwanger Bach: Vent: pH: 7.2 - 7.99; pCO$_2$: 3426-10715 µatm; temperature: 8.4 - 9.0°C; Alkalinity: 4.4 - 5.22 meq/L; Mg/Ca: 0.4-0.7; δ^{18}O$_{H2O}$: -9.9‰ SMOW. Westerhöfer Bach: Vent: pH: 7.3 - 7.6; pCO$_2$: 6760 - 11481 µatm; temperature: 8.8 - 9.4°C; Alkalinity: 5.4 - 5.84 meq/L; Mg/Ca: 0.4 - 0.5. Climate: temperate oceanic. Deposits: calcitic crusts on cyanobacteria-dominated biofilms	Neomorphism and cementation	(Arp et al., 2001, 2010; Shiraishi et al., 2008; Brinkmann et al., 2015)
Edipsos hot springs (Euboea, Greece)	Recent ferrous hot springs along NNE-SSW and NW-SE to E-W extensional lineaments. Cooling magmatic intrusions present in subsurface, related to Plio-Pleistocene back-arc volcanic center. Na-CL type spring fluids (T: 43.9 - 82.2°C; pH: 6 - 6.8; TDS: 18800 - 33735 mg/L; Mg/Ca: 0.2 - 2.6; HCO$_3^-$: 489 - 691 mg/L). Climate: cold semi-arid (Mediterranean). Deposits: Spring mounds with vent to distal slope facies deposits (aragonite and calcite) including dense crystalline crusts, coated gas bubbles, rafts, shrubs, ooids, cemented microbial filaments, allochtonous travertine together with iron oxides and minor halite, gypsum.	Neomorphism, cementation, dissolution, shrinkage	(Kanellopoulos, 2012, 2013; Kanellopoulos et al., 2016)

Table 1

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Case	Age	Process	Rates	How determined?	Reference
New Grassy Spring, (Mammoth Hot Springs, Yellowstone National Park, USA)	Recent	Calcite rhombs growing over and encasing aragonite needles that precipitate around filamentous *Aquificales*	Days - weeks to 5 years	SEM of recent precipitates; ^{228}Ra/^{226}Ra	Personal observations; (Sturchio, 1990)
Bagni san Fillipo (Italy)	Recent	Aragonite to calcite neomorphism (inversion) in hot spring deposits	10 - 15 days	Observations and mineralogy identification over time	(Malesani and Vannucchi, 1975)
Cave pearls in active underground limestone mine (Quincy, IL, USA)	Recent	Neomorphism (recrystallization) of laminated micritic-microsparitic couplets into equant calcite spar.	Onset in 1 – 2 months	Petrography of in-situ experiments (precipitation on limenstone substrates)	(Melim and Spilde, 2011)
Deinschwanger Bach tufa (SW Germany)	Recent	Aggrading neomorphism (recrystallization) of micritic-microsparitic precipitates and cementation by elongated calcite spar crystals	4 months to 2 years	Petrographic comparison of recent and older parts of the tufa crusts	(Arp et al., 2001)
Hydrobia Beds (Mainz Basin, Germany)	Miocene/ Recent	Neomorphism (recrystallization) of high-magnesium to low-magnesium calcite by recent meteoric water infiltration	10 - 20 years	Sampling over course of years, linear extrapolation of rates	(Koch and Rothe, 1985)
Juxtlahuaca Cave (Sierra Madre del Sur, Mexico)	Holocene	Partial to complete inversion of aragonite to calcite in a cave stalagmite. Calcite occurs as layers, isolated lenses, irregular zones and dispersed euhedral crystals.	12 – 271 years	U/Th age comparisons between multiple aragonitic and calcitic layers with a strict stratigraphic control	(Lachniet et al., 2012)
Glamouse Cave (France)	Holocene	Aragonite to calcite neomorphism (inversion) in speleothem	1000 ±350 years	U/Th dating	(Frisia et al., 2002)
Fall Creek cold spring (Alberta, Canada)	Holocene	Aggrading neomorphism (recrystallization) and isopacheous, trigonal and mosaic calcite cementation	~5000 years (oldest deposits); 310 ±50 years (youngest deposits)	^{14}C dating on embedded wood + ^{14}C dating on bison bone in adjacent spring	(Rainey and Jones, 2007)

Table 2