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

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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 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 detangle 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 of non-marine carbonates.

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). Several non-marine carbonate fabrics have been recognized in subsurface lithologies of economic interest (Harris, 2000; Shiraishi et al., 2008b; Della Porta, 2015; Ionescu et al., 2015; Wright and Barnett, 2015; Schroeder et al., 2016; Claes et al., 2017a; Mercedes-Martín 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), offering researchers the chance to improve approaches to detection of ancient and extraterrestrial life. 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 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

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responsible for carbonate formation, and it never really stops. This is the inescapable conclusion from many, recent 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 diagenesis (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; Moore and Wade, 2013; James and Jones, 2015).

We define 'non-marine carbonates' here 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 (Figs. 1, 2). Non-marine carbonates are primarily located in continental settings, with some on islands (Benzerara et al., 2010; Kremer et al., 2012; Ionescu et al., 2015). The following deposits are included in this review under this heading (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, with less focus on biogenic carbonate deposits such as ostracod, gastropod or bivalve beds, is selected (Fig. 1, Table 1), to illustrate common early diagenetic processes in these deposits and environments.

In view of their application in paleoclimatic reconstructions, most research has been published on Recent to Quaternary deposits. Non-marine carbonates have however 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 Kranenkonk, 2007; Awramik and Buchheim, 2009; Fairchild et al., 2016). Given the focus here on the early stages of diagenesis, the examples most often referred to, 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, 2001). 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
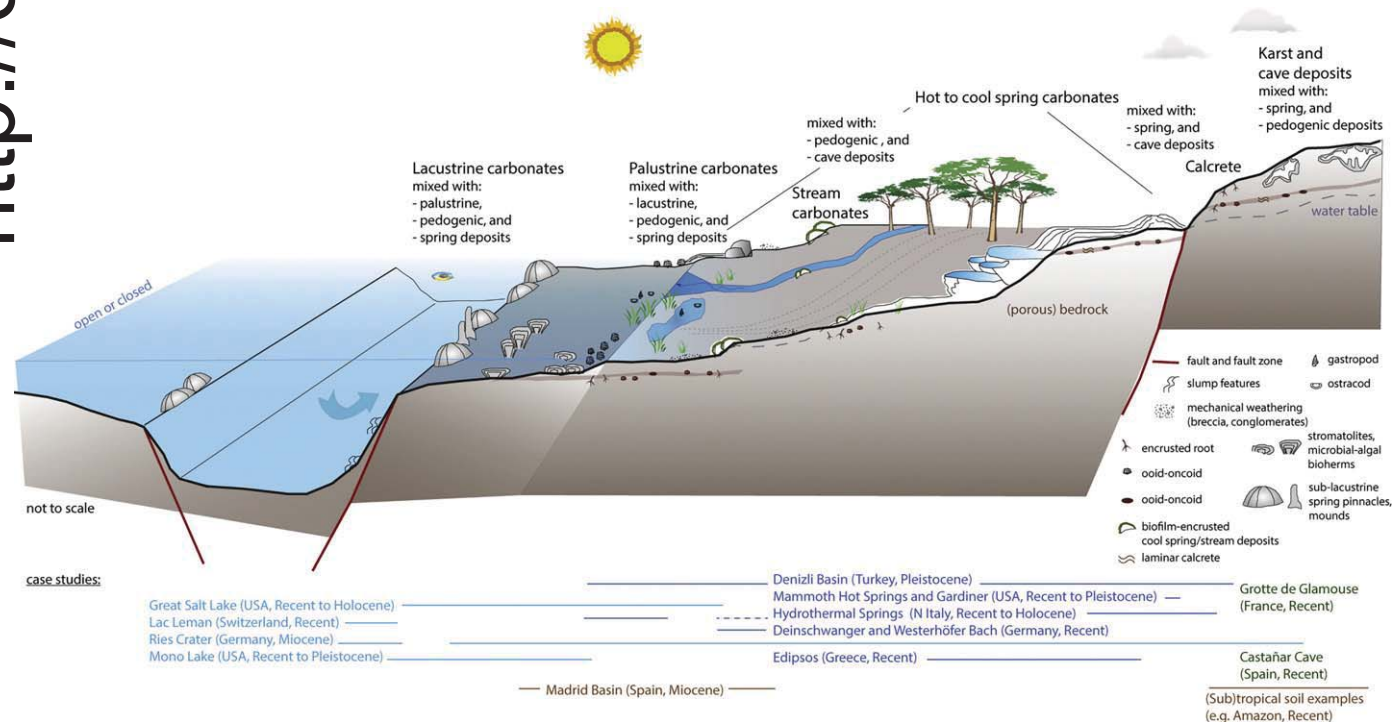

Fig. 1. Schematic drawing and cross-section of the location and transitions between different non-marine depositional environments and their deposits (based on Freytet and Plaziat, 1982; Arp, 1995; Pedley and Rogerson, 2010; Brasier, 2011; Wright, 2012; Della Porta, 2015) considered in this review. The extent of the reference examples of Table 1 is indicated below the cross-section.
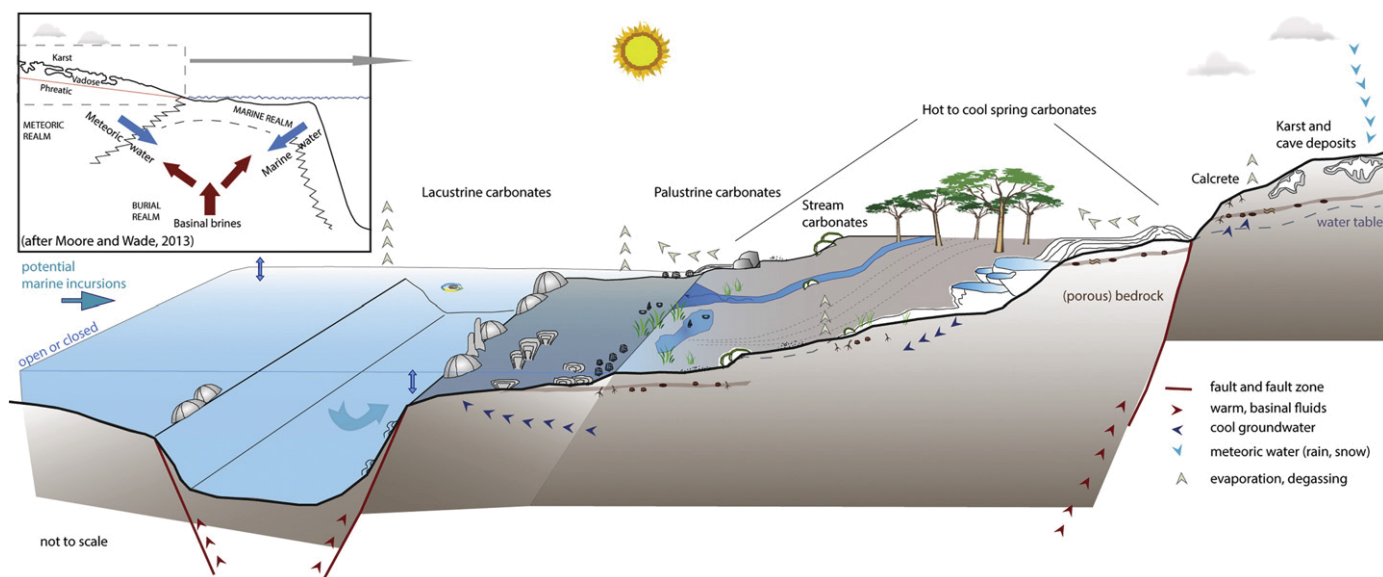
Fig. 2. Schematic drawing and cross-section showing fluids involved in formation and early diagenesis of non-marine carbonates. Early diagenesis may take place from marine influenced, evaporative fluids over freshwater and fluids that have migrated up from the deep(er) subsurface at, for example hot springs.

marine-meteoric and subsurface, or burial, diagenetic fluids (Fig. 2). In this view, water chemistry, water flux, temperature and pressure of rock-water interactions 'drive the diagenetic processes' (Moore and Wade, 2013).

Neither of these approaches really suits or adequately allows describing 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). Further, diagenesis of non-marine carbonates is not always driven by low ionic strength meteoric waters, as illustrated in Fig. 2.

It is therefore something of an oversight that the range of early diagenetic conditions (fluid composition, temperature, biology) and processes are 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. Several 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 1 mm 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 diagenesis' refers to those rock fabric altering processes and transformations that take place or start during and just after deposition.

2.1. Summary of (primary) non-marine carbonate fabrics, mineralogy and processes of crystal formation

2.1.1. Primary 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', not yet diagenetically altered, carbonate products. In many of these cases, the presence and potential influence of (early) diagenetic processes on the fabrics is however not explicitly addressed.

Table A2 provides a summary, including references from field and laboratory studies, of several common carbonate mineralogies in non-marine deposits. The initial mineralogy and fabric are important as they will influence 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.

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, on the exact $CaCO_3$ polymorph that forms, plus the 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 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

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.

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. (2013a, 2013b, 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 (>550 m 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)

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Table 1 (*continued*)

Non-marine carbonate environment	Description of setting, water chemistry and depositional facies	Early diagenetic processes described	References
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 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; $\delta^{18}O_{H2O}$: -5.9 to -6.5‰ SMOW. Deposits: stalagmites and flowstones of aragonite and calcite mineralogy	Neomorphism, local dissolution related to organic matter decomposition	Frisia (1996), Frisia et al. (2002)
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, 2015a)
Spring and streams			
Denizli graben (SW Turkey)	Pleistocene spring carbonate mound and lacustrine deposits along extensional and transtensional graben faults. Recent spring water composition at Pamukkale: Ca-Mg-SO₄-HCO₃-type, 35–57 °C (vent) to 20 °C downstream, pH: 6.0–7.8. Deposits: spring mounds (up to 40 m high to 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. (2017), 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, 2017a, 2017b), 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-HCO₃-SO₄ -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 evaporites. Water chemistry of active springs (strongly variable depending on subsurface pathways): Ca-HCO₃-SO₄ -type, pH: 6.0–7.15; Temperature: 17.1–65 °C, pCO_2: -1.83 - 0.82; Mg/Ca: 0.3–0.5, $\delta^{18}O_{H2O}$: -6.7 to -10.6‰ SMOW. Climate: Humid subtropical and oceanic (today). Deposits: Forming isolated masses up to 40–50 m thick and 5 km². 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; $\delta^{18}O_{H2O}$: -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. (2008a, 2008b), Brinkmann et al. (2015)

Table 1 (*continued*)

Non-marine carbonate environment	Description of setting, water chemistry and depositional facies	Early diagenetic processes described	References
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)

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, sulfate 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 early, nano-scale phase changes.

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 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, $CaC_2O_4 \cdot H_2O$) or as polyhydrates (weddellite, $CaC_2O_4 \cdot nH_2O$, $2 \leq n \leq 3$). 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 weddellite, 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 a Scanning Electron Microscope (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 'Needle Fibre Calcite' (NFC). This common fungal hyphae-related fabric (Wright, 1986), 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) (Martín-Pérez and Košir, 2017). Verrecchia et al. (1993) showed that short crystals and spikes surrounding the exterior of the calcified fungal filaments in some Quaternary calcretes of Israel had compositions better compatible with calcium oxalates than with calcite and that most needles and mineral encrusted fungal hyphal walls had intermediate compositions.

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. 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.

2.2.2. The role of micro-organisms and organic matter in carbonate crystal formation

Mostly based on in-vitro laboratory experiments, recent advances have been made in unravelling the different, microbial-related and organic matter (degradation) processes that facilitate and localize carbonate crystal formation. 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 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., 2008a, 2008b; 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
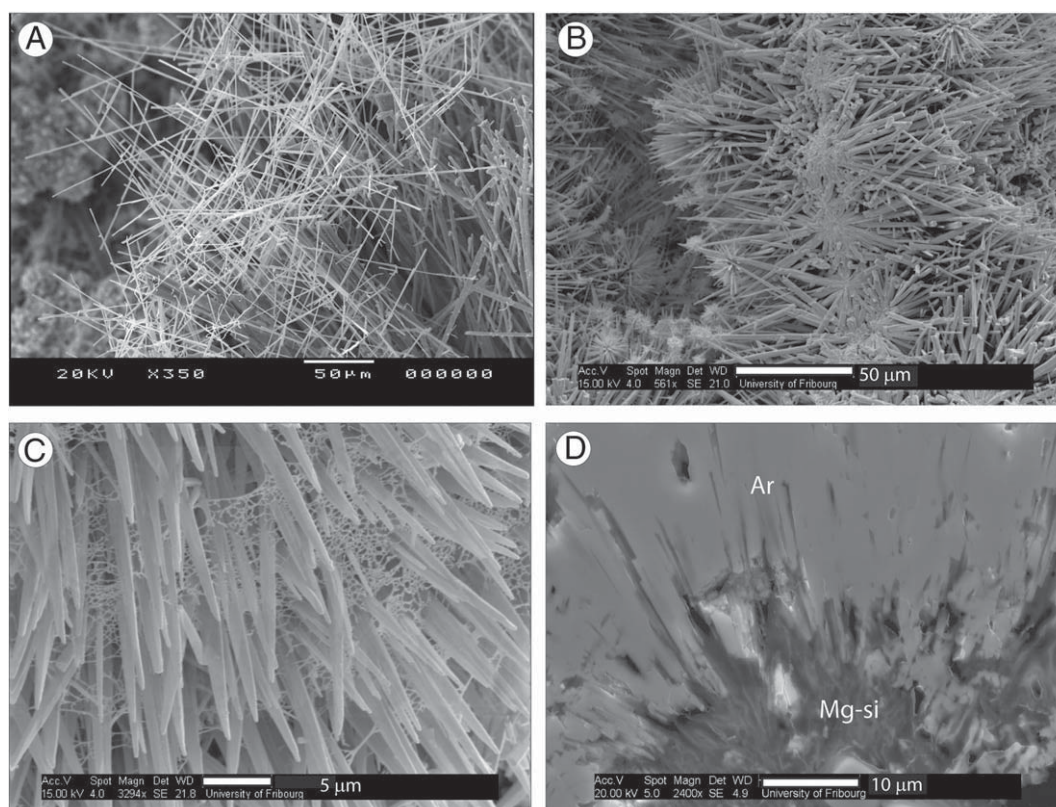
Fig. 3. Precipitation and early diagenesis in the micro-environment. (A) Porous aggregates of straight monocrystalline Needle Fibre Calcite (NFC) crystals from a moonmilk speleothem of Koselevka cave, Slovenia. SEM image, secondary electrons mode (Image: courtesy of Dr. A. Martín-Pérez; Martín-Pérez 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 <100 kyr difference in age, all Mg-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).

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 also encourages processes at the cell wall-pore fluid interface during early diagenesis, in particular in association with the degradation of organic matter (e.g. by sulfate 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 at the expense of primary unstable and/or amorphous phases. Experimenting with microbial isolates from Altamira cave in Spain, Sanchez-Moral et al. (2003) demonstrated that metastable phases such as vaterite and/or monohydrocalcite formed first. Such metastable phases can then be easily transformed into calcite phases.

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 then 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

A last, recently extensively studied process involves the intimate interaction between carbonate and silicate phases during precipitation and early diagenesis. 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 now shown that the formation of Mg-silicates from a primary solution evolves through poorly crystalline intermediates (Jones, 1986; Tosca et al., 2011). In particular Tosca and

Masterson (2014) have proven that the loss of interlayer sites and surface hydration drive the change of poorly crystalline phases (Mg-silicate 'gels') into crystalline Mg-silicate minerals. Mg-silica precipitation may furthermore change the brine fluid composition, lowering the Mg/Ca ratio of the precipitating fluids and as such favour 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 surrounding, open pore space, facilitating aragonite precipitation.

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, 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 formation 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 (recrystallization) 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 transformed into 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 equally observed in Recent and Holocene travertine sequences at Mammoth Hot Springs (Yellowstone National Park, USA) (Fouke et al., 2000; Chafetz and

Guidry, 2003; Fig. 4A-C). The relics may preserve the initial mineralogy or be merely textural. In other cases, inversion of aragonite may result in a nearly complete destruction of the primary fibrous fabric, leading just to inclusion-rich elongated, calcite cements (Arp et al., 2013a; Martín-García et al., 2014; Frisia, 2015).

Inversion 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 (Frisia et al., 2002; Domínguez-Villar et al., 2017). This may result from short (intra-seasonal) to longer timescale (inter-annual or permanent) modifications of the precipitation conditions or pore fluid composition (e.g. concentration of CO_2, water discharge, prior precipitating phases) (Domínguez-Villar et al., 2017). Based on high-resolution 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 then took place in parallel with inversion of aragonite when the aragonite saturation decreased. Transmission Electron Microscopy (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, 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 and Verrecchia (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 organic or micritic matter as inclusions outlining primary lamination and textures. This model was partially disputed by Brasier et al. (2015) 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.

Neomorphism can potentially rapidly modify the primary fabric and texture. Several authors also suggest that any 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). (Aggrading) neomorphism is therefore 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
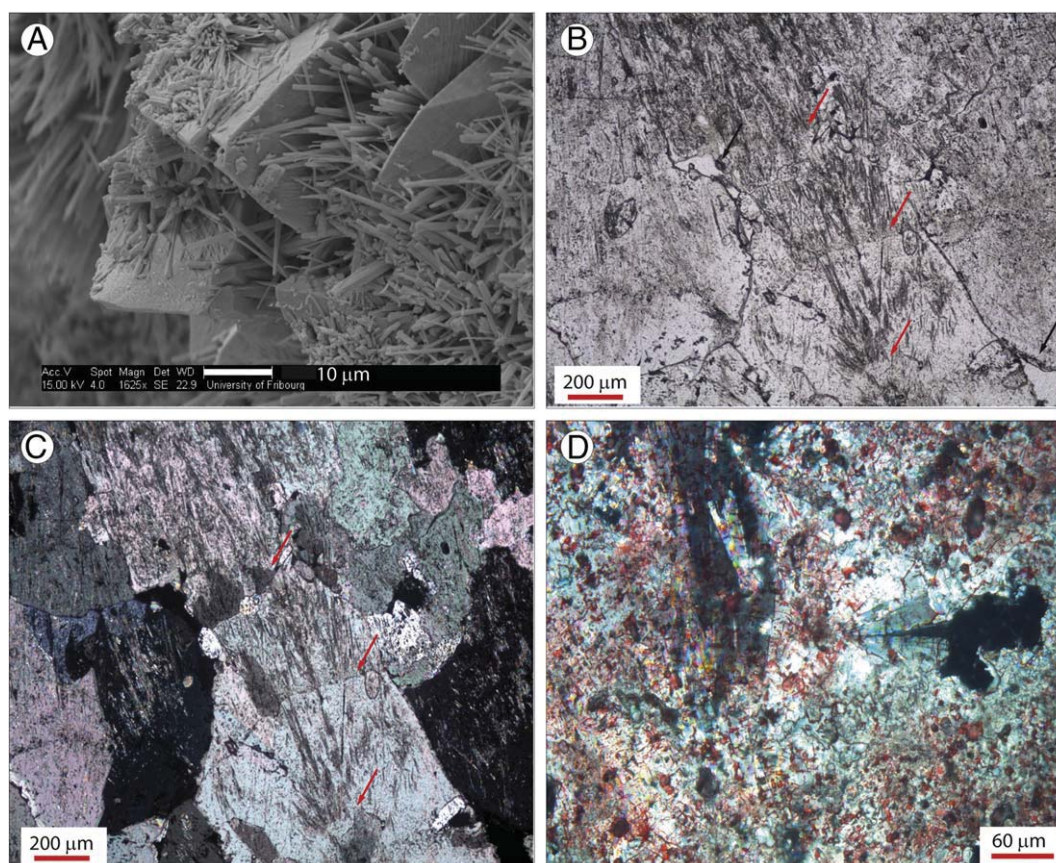
Fig. 4. Neomorphism. (A) Calcite rhomb crystals, consisting of different platelets, are encasing and growing outward from aragonite needles in an encrusted filamentous mat sample at the transition between the Apron-Channel and Pond Facies (Fouke, 2011) of the active New Grassy Spring at Mammoth Hot Springs (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).

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 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 (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 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. These authors 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 (Chafetz and Guidry, 2003; Pentecost, 2005; Rainey and 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 (Figs. 4A, 5C) and may take place contemporaneously, at different depths (Martín-García et al., 2014), or these processes may alternate through time 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), such as microbial build-ups of 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 diagenesis. This means the 'original' and

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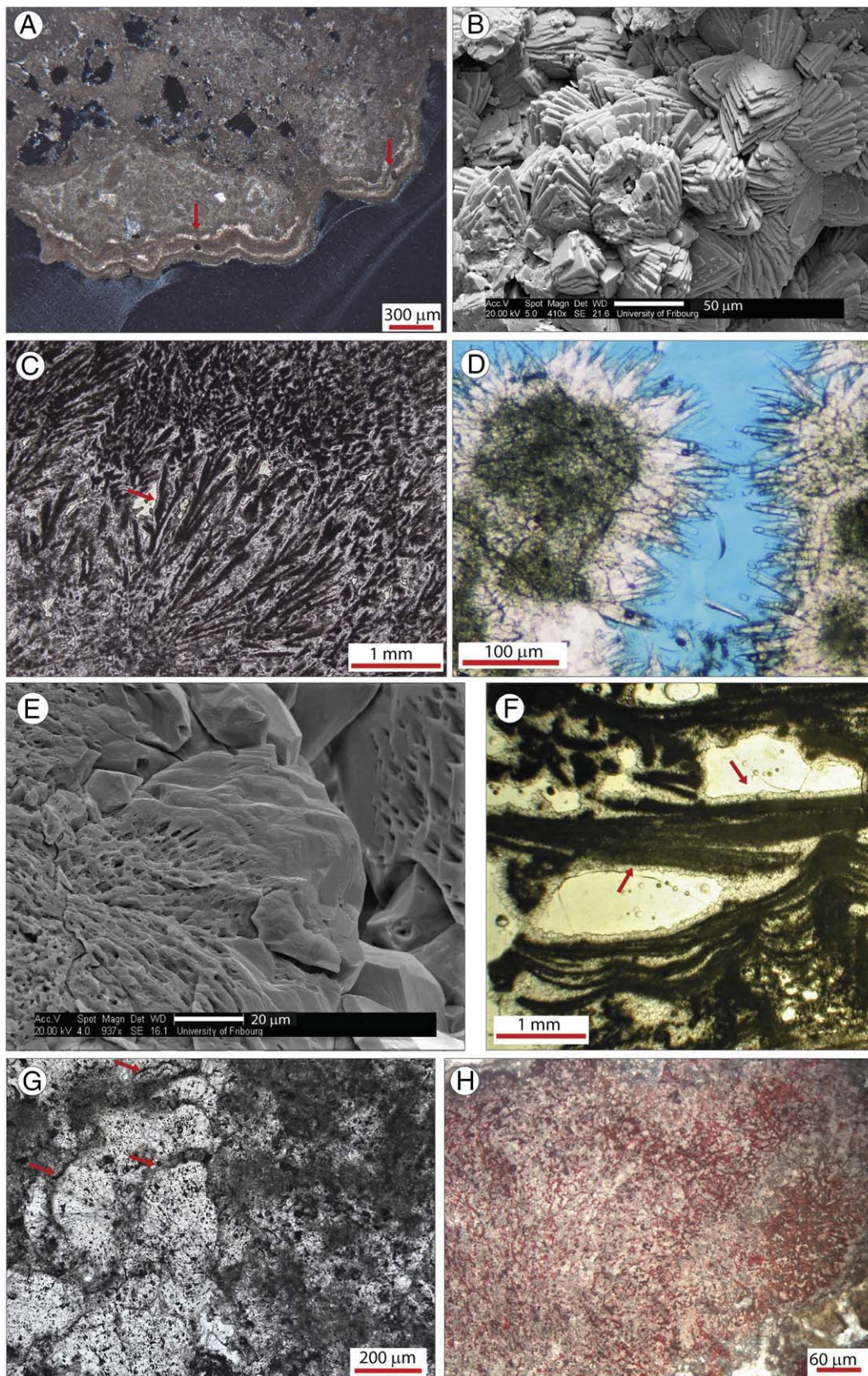
'diagenetic' water geochemical signals may be indistinguishable (Andrews, 2006).

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) demonstrated, already early, 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 (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 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 other, 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.

2.6.1. Replacement

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 h 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 ($CaCO_3 \cdot 6H_2O$) 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 sulfate 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; 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 SiO_2) and both pH (~6 to >9) and temperature are strongly fluctuating (Fig. 6B, C),

Fig. 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. 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).
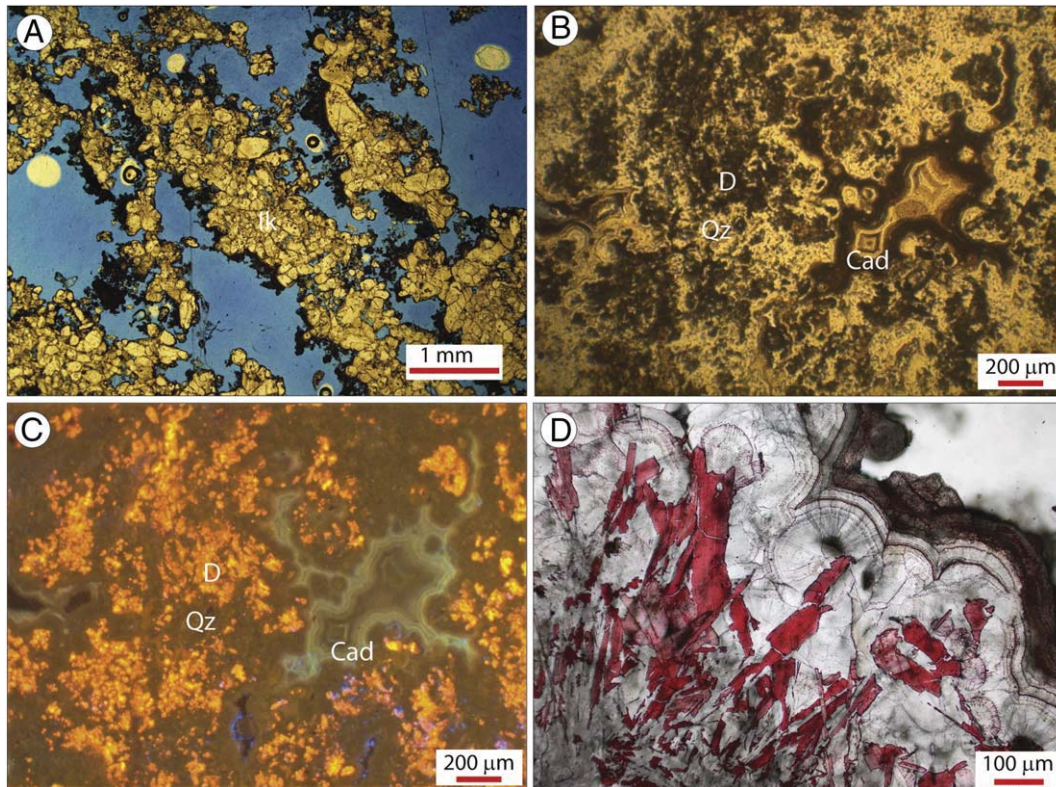
Fig. 6. Replacement processes. (A) Transmitted light image of calcite pseudomorphs after ikaite (Ik; large, clear nicely shaped crystals) leaving a porous fabric behind (blue resin is pore space) (north shore of Mono Lake, USA). (B) and (C) Transmitted light and cathodoluminescence image of extensively 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).

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 (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, 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 the replacement processes (Folk and Pittmann, 1971), possible (biogenic) silica sources and the 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

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

Fig. 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 numerous publications and books (Allan and Matthews, 1982; Morse and Mackenzie, 1990; Hoefs, 2004; Sharp, 2007; van Dongen
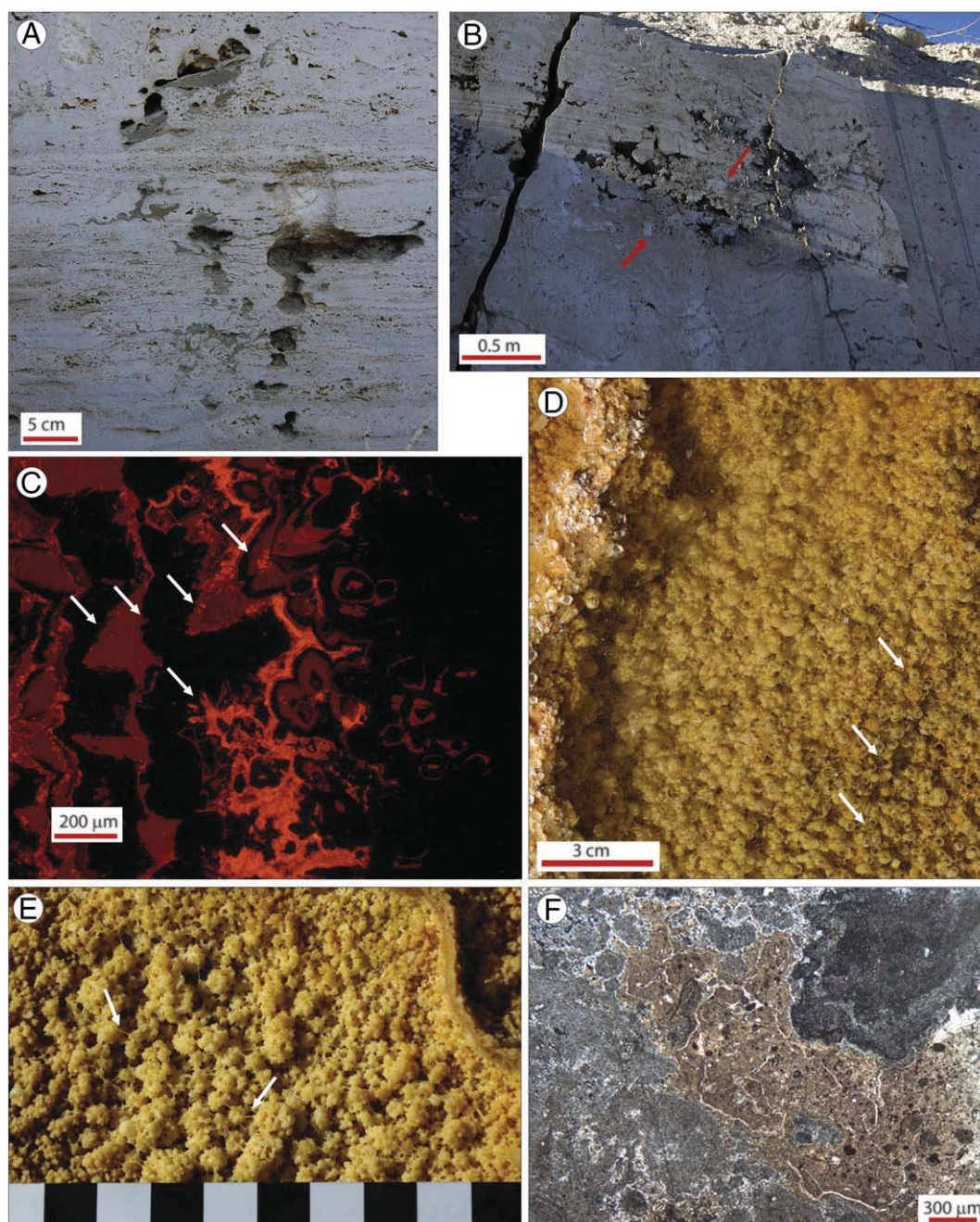
Fig. 7. Weathering processes. (A) Dissolution cavities and vugs with clayey infill in Pleistocene Distal Slope travertine (encrusted gas bubbles, fossilized microbial and algal mats) (Gardiner area, USA). (B) Large dissolution cavity showing, cemented angular travertine clasts (arrows) resulting of collapse 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).

et al., 2007; Moore and Wade, 2013; Swart, 2015) and several processes and trends are indicated in Fig. 8.

The range of non-marine carbonate 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 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
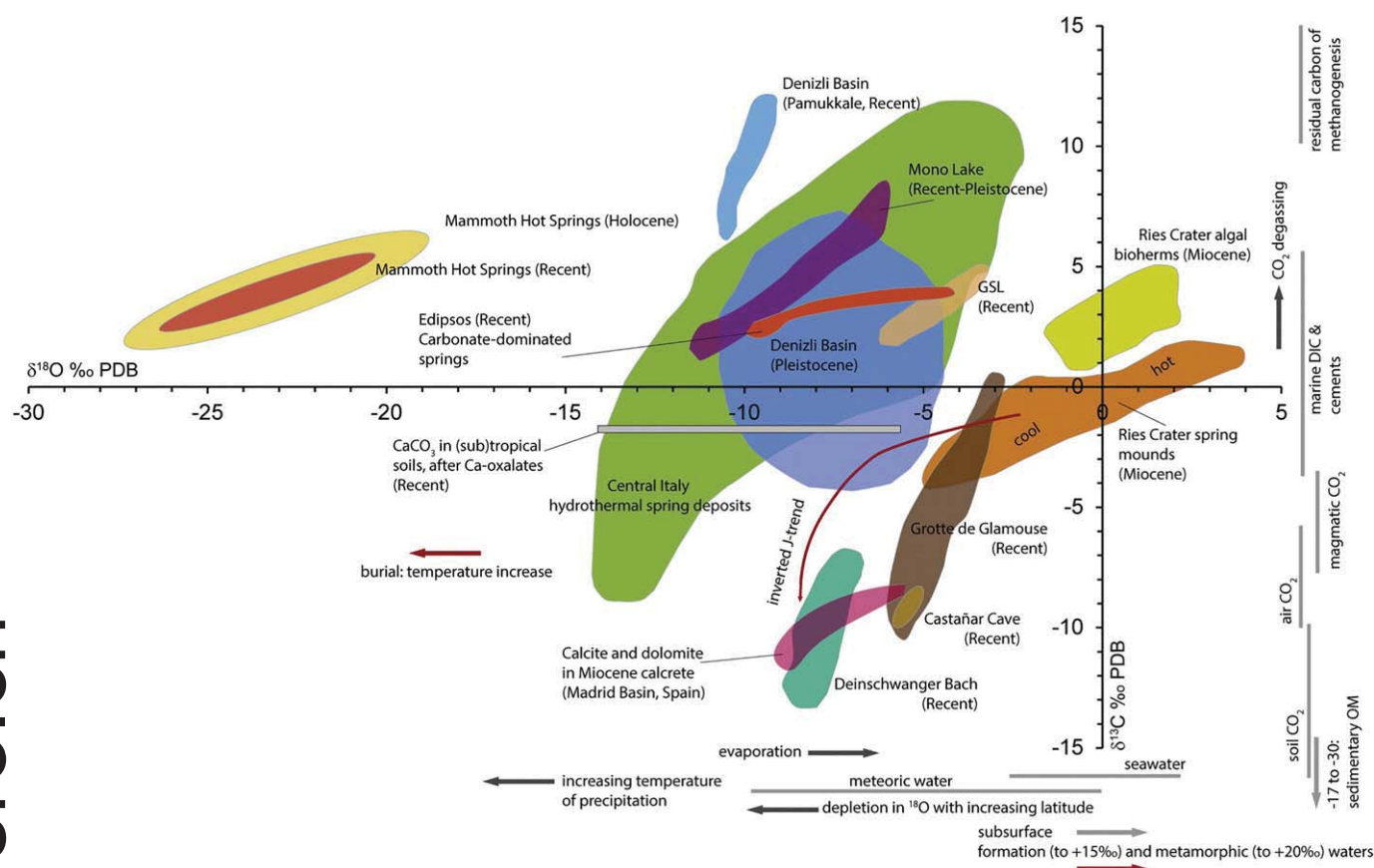
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Fig. 8. Compilation of δ¹³C and δ¹⁸O values in non-marine carbonate case studies (see Table 1) showing the great variation in stable isotopic signatures. Isotopic signatures of common water and carbon sources in the non-marine environment are outlined (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 CO₂ (Lohmann, 1988). The covariance of δ¹³C and δ¹⁸O in many non-marine carbonates relates to simultaneous processes of CO₂ 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 δ¹⁸O available for calcite; GSL = Great Salt Lake.

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 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 δ¹³C–δ¹⁸O 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 investigated in field samples or lab precipitates (Martín-García et al., 2009; Domínguez-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 final 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 carbonate deposits on their 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 $\delta^{13}C$ values are more conserved than are $\delta^{18}O$ 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 (Wassenburg et al., 2012). In their study of Recent precipitates and paleo-riverine tufa deposits, Janssen et al. (1999) remark on a shift in $\delta^{13}C$ and $\delta^{18}O$ values. For both isotopes they observe that paleodeposits show less variability and a shift towards higher values (<1‰ V-PDB for $\delta^{18}O$; 1.5‰ V-PDB for $\delta^{13}C$). 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, 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 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). 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 (Ritter 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 also be estimated.

So far there have, however been few studies examining the exact 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), for example, 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

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 and Verrecchia, 1998; Janssen et al., 1999; Chafetz and Guidry, 2003; Brasier, 2011; Brasier et al., 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 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), a short, non-exhaustive list, can be compiled:

- Fabric changes unequivocally related to variations in depositional conditions such as temperature, flow rate (Fig. 9A, B).
- Fabrics that are influenced by heterogeneities related to depositional processes: e.g. pellets, grains or micrite that become 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 or 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.
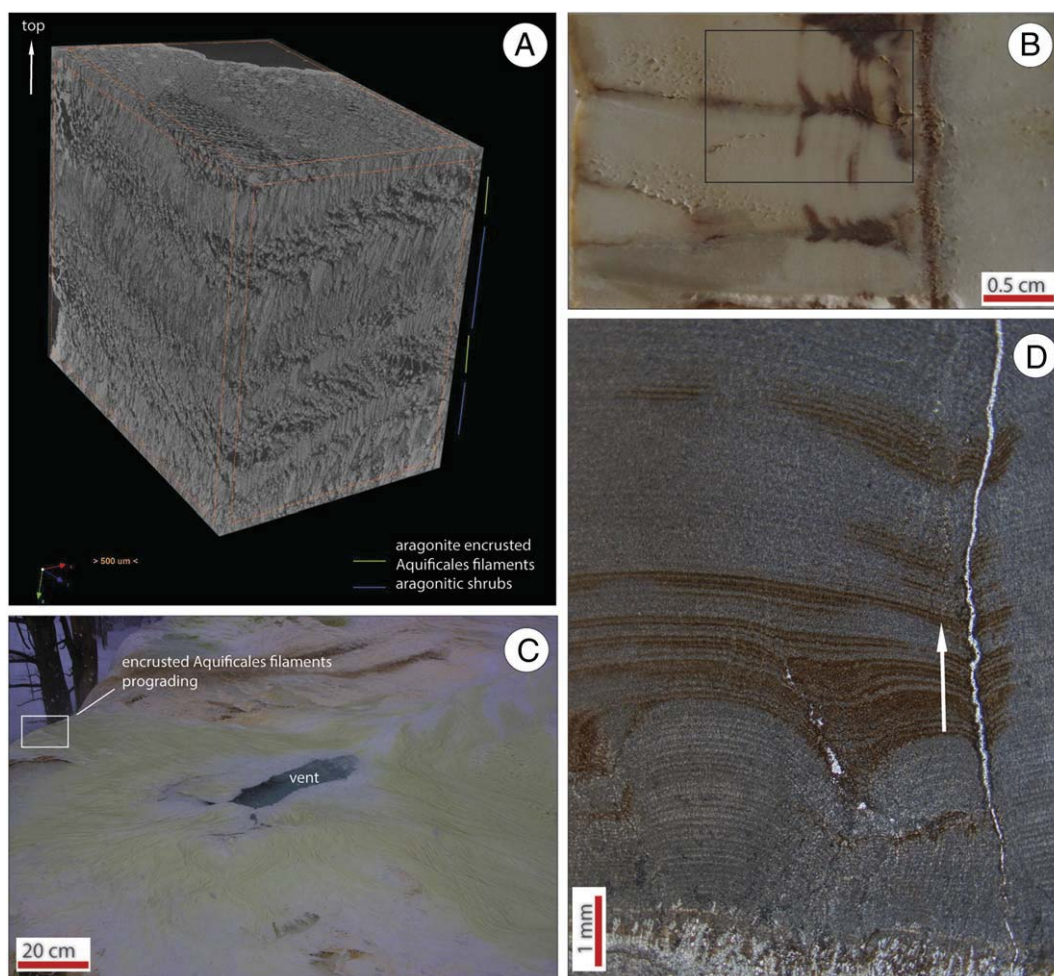
Fig. 9. Primary fabrics? (A)-(B) 3D reconstructed volume, based on micro-computer tomography (μCT) of a Proximal Slope sample from an inactive spring (Skyscan 2211, 9.2 μm resolution). Alternating laminae of aragonitic shrubs, growing perpendicular to the slope, and aragonite-encrusted *Aquificales* 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.

None of these petrographic features 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 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 or 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

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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 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 and Verrecchia (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) dominantly shows only coarse, sparry equant to radial, elongated crystal fabrics (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). 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 identified (Bajo et al., 2016).

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 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, 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 bioerosion 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 - again - 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 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,

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

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 limestone 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)

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, related 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 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 addressing non-marine carbonate diagenesis?

From the broad range of early 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 dissolution and minor cementation from meteoric waters (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, their diagenetic processes and drivers and fluids (Alonso-Zarza, 2003; Brasier et al., 2015; Della Porta, 2015). Each corner of the front triangle in Fig. 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 (inversion and recrystallization) processes are placed between cementation and dissolution. Several of the early diagenetic microscopic to macroscopic fabrics and textures discussed earlier in the text, are located and illustrated in the diagram. 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 includes 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 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.

Several gaps, however, remain in our understanding of the mechanisms and illustrated processes that transform primary, non-marine sediments and precipitates during syn- and post-depositional, (very) early diagenesis, into the rocks found and studied in the geological record and how this could (or not) affect the paleoclimatic archives preserved in them. Focused case studies, where observations and monitoring of active carbonate deposition can be integrated with exposed or subsurface fossil deposits, 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 detangle the exact diagenetic pathways (Ritter et al., 2017), controlling parameters and rates of individual processes, across the continuum of non-marine carbonate depositional contexts. A better understanding of the 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 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 rock record of possibly diagenetically modified carbonate deposits, used - or not - in paleoclimatic and -environmental studies.

5. Final thoughts

(Early) diagenesis in non-marine carbonates is a broad topic, touching several other domains and research questions that could not be
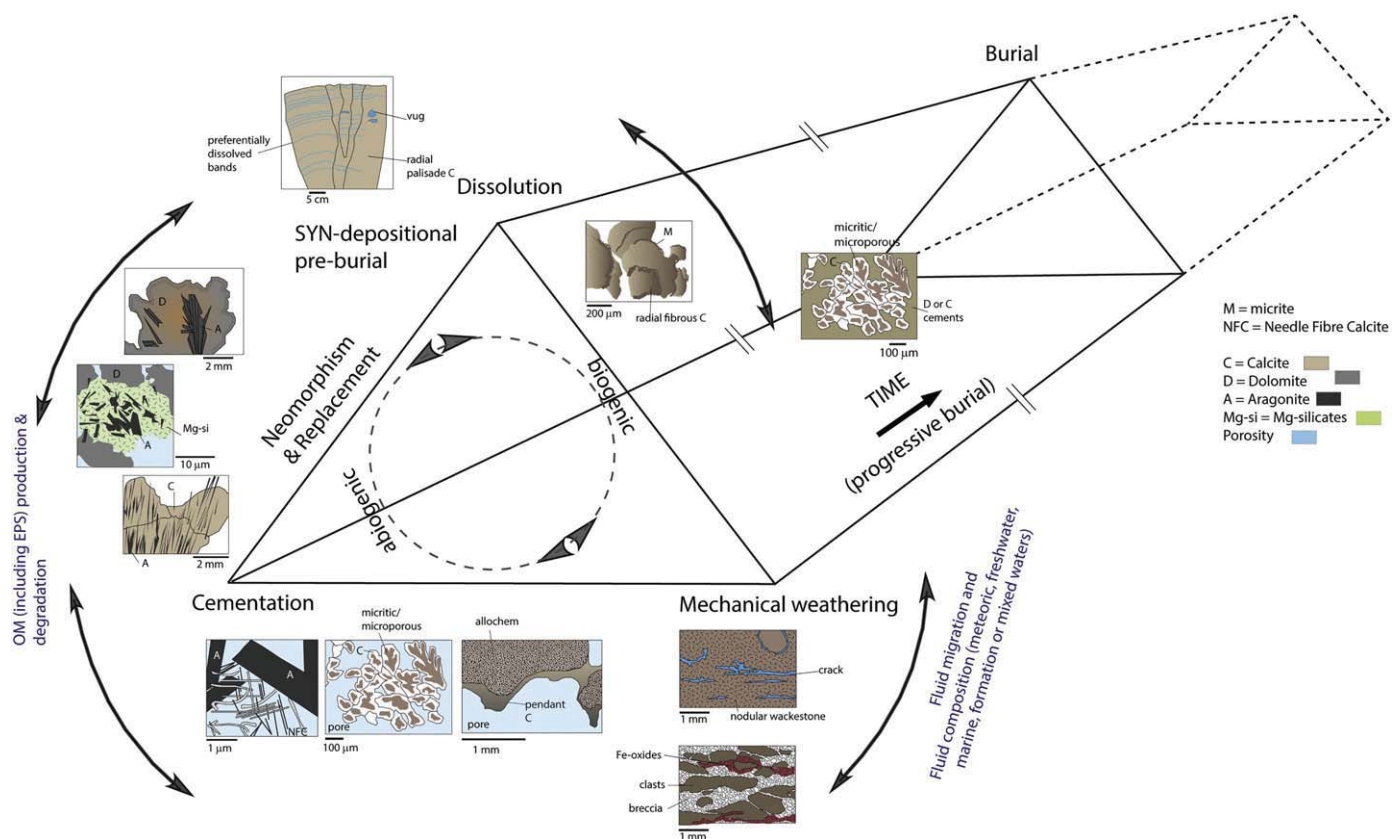
Fig. 10. A pyramidal, process-centered framework for understanding and addressing non-marine (early) carbonate diagenesis. For full explanation, the reader is referred to the text. A number of fabrics discussed in the text and related to the different 'end-member' diagenetic processes, marking the corners of the frontal triangle, are schematically illustrated.

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 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 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
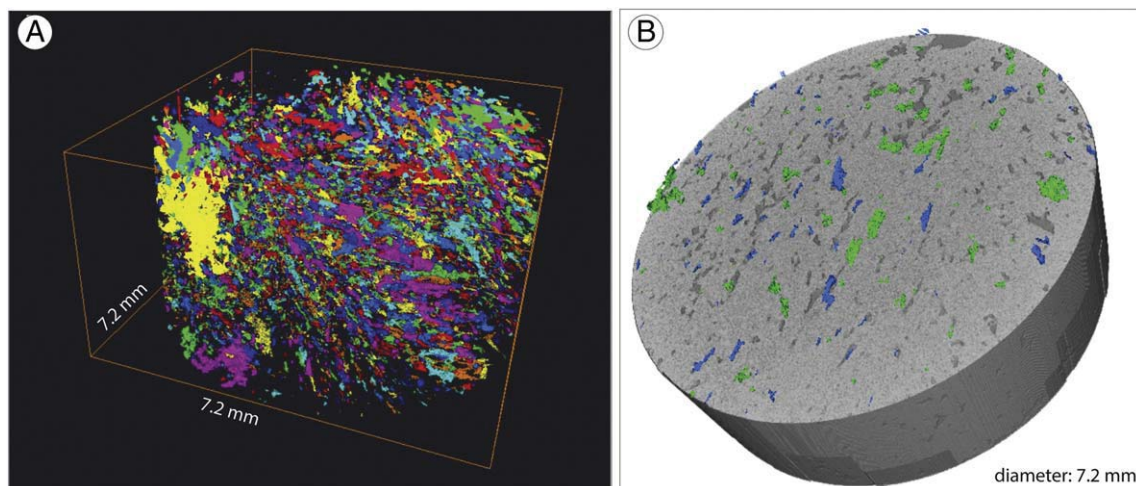

Fig. 11. Micro-computed tomography (μCT) to study 3D properties of diagenetically altered fabrics. (A) Color labeled pore space in Pleistocene spring carbonate pervasively cemented by an isopachous calcite rim (Cakmak quarry, Denizli Basin, Turkey). Each color marks a separate pore space, not connected 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).

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 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 micro-organisms 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.
- 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 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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sedgeo.2017.09.011.

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