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Invited review

High spatial resolution investigation of nucleation, growth and early diagenesis in speleothems as exemplar for sedimentary carbonates

Silvia Frisia[a,*], Andrea Borsato[a], John Hellstrom[b]

[a] School of Environmental and Life Sciences, The University of Newcastle, Callaghan, New South Wales 2308, Australia
[b] School of Earth Sciences, The University of Melbourne, Parkville, Victoria 3010, Australia

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ABSTRACT

Investigation by high resolution Transmission Electron Microscopy (HR-TEM) and Synchrotron-Radiation based micro X-ray fluorescence (SR-μXRF) of diagenesis in carbonates imposes uncertainties on the boundary between stages of crystal growth and post-depositional processes. Speleothems and dolomite are exemplars of the entire range of processes that result in solid materials consisting of crystals. HR-TEM investigation of speleothems suggests that there are many possible pathways of crystallization comprising classical ion-mediated, particle-mediated and formation of metastable phases. Diverse pathways influence the potential of a primary carbonate to undergo post-depositional transformation, with consequences on the accuracy of the preservation of original chemical and physical properties. The capability to date speleothems with U-series techniques is unique amongst other archives of Earth's history. It has been observed that U mobilization, which results in age inversions and uncertainties, is dependent on both crystallization and diagenetic pathways. Here, it is also proposed that the presence of organic colloids, mostly consisting of humic substances (HS), influences the extent to which U may be mobilized, as well as the capacity of original speleothem fabric to undergo dissolution and re-precipitation. Our hypothesis that colloidal HS protect the initial products of crystallization from subsequent diagenesis could explain the existence of primary dolomite preserved in Triassic sabkha facies influenced by fluvial input of siliciclastics. Primary dolomite nanocrystal aggregates coexist with single crystals, highlighting that multiple formation mechanisms were possible, which explains the variety of micro and nanostructures observed by conventional TEM investigations in dolomites. Similarly, we observed calcite nanocrystal aggregates and single crystals preserved in Triassic shallow marine facies, which are famous for their preservation of original aragonite, influenced by continental siliciclastic input. Our new data on the Triassic carbonates suggest that when HS colloids are abundant, nanocrystal aggregates are commonly preserved, possibly because of a protective coating by organic substances. These hinder both the transformation of the aggregates into larger crystals and multiple-steps diagenetic transformation that obliterate primary environmental signals.

As opposed to textbook assumptions, it is here proposed that the existence of multiple crystallization pathways for carbonates within the same depositional environment, such as a cave setting or a sabkha, have repercussion on the early diagenetic processes and the extent to which diagenesis significantly resets the original chemical and physical signals. By using speleothems as paradigm for carbonates formed in natural environments where organic compounds are ubiquitous, the present review corroborates the notion that most mechanisms of carbonate crystallization, when the carbonate is not a biomineral, follow inorganic pathways. However, the role of organic substances, as inhibitors of growth and diagenesis, has profound influences on preservation of initial states of crystal formation.

1. Introduction

1.1. *Early diagenesis of carbonates speleothem contribution to redefining the concept*

Early diagenetic processes potentially change fabrics, mineralogy, and the microstructural and chemical properties of carbonates that are commonly used to reconstruct and date Earth's past history (see, for example: Allan and Matthews, 1982; Frisia, 1994; Frisia and Wenk, 1993; James and Choquette, 1990; Scholz et al., 2004; Swart, 2015; Webb et al., 2009; Zhang et al., 2014). Despite the abundance of process research, early transformation changes subsequent to carbonate

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* Corresponding author.
E-mail address: silvia.frisia@newcastle.edu.au (S. Frisia).

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deposition keep eluding our capacity of detection with standard inquest methods. In Berner's (1980) definition of early diagenesis, there is emphasis on systematically describing and modelling changes that occurred soon after "*arrival of a particle at the sediment/water interface*" until "*burial to a few hundred of metres where elevated temperatures are not encountered*". Early diagenesis of carbonates, however, encompasses a wider spectrum of processes. In many cases, carbonates are biogeochemical or chemical precipitates, and not particles deposited at the sediment/water interface, which, in the majority of studies, is assumed to be marine water (Berner, 1980; Morrow and McIlreath, 1990). In this common presumption, the first stages of carbonate diagenesis should be dissolution and re-precipitation in a meteoric environment, which has a much lower Ion Activity Product (IAP) and lower supersaturation for aragonite (or calcite, or dolomite) than seawater (Morse, 2003). Consequently, sediments exposed to natural seawater are believed to be affected by little early diagenetic alteration (Berner, 1980), if no other processes contribute to alter the pH or alkalinity (Morse, 2003).

Continental carbonates, and in particular cave speleothems (stalagmites, stalactites and flowstones), although relatively rare compared to their marine equivalents, have been recognized as one of the most powerful archives of past global climate and environmental changes (Henderson, 2006; Hu et al., 2008; Wang et al., 2008; Vaks et al., 2013). In these continental carbonates, diagenesis is not a desirable process, as it may re-set the original climate signals (Fairchild and Baker, 2012; Scholz et al., 2014). Oxidation of organic matter, which is present in variable amounts in most speleothems (Ramseyer et al., 1997), for example, causes dissolution particularly if associated to the presence of fluids in porous fabrics (Genty et al., 2002). Carbon dioxide generated by organic matter oxidation is sufficient to cause under-saturation in pore waters relative to aragonite and calcite, resulting in transformation and recrystallization (Frisia, 1996). Bacterially mediated processes also have been found to play a role in early diagenesis as bacteria oxidise organic matter (Morse, 2003) and induce cementation (Folk and Chafetz, 2000; Frisia, 1996), or promote dissolution and re-precipitation (Frisia et al., 2012).

In Berner's (1980) definition of early diagenesis, there is the assumption that particles settled at the sediment/water interface are then exposed through time to an environment that has different physical and chemical characteristics with respect to those of the depositional setting. By contrast, speleothem growth and subsequent modifications usually occur in the same meteoric, vadose environment under similar physical and chemical parameters (De Boever et al., 2017). Speleothems, therefore, defy the accepted concept of early diagenesis. In speleothems, research on crystallization pathways responsible for the variety of fabrics observed has, to date, relied on classical nucleation theories. In the classical nucleation and growth approach, supersaturation of the parent solution controls the growth mechanisms of crystals from a solution (Sunagawa, 2005). This assumption led to the notion that columnar calcite crystals, which commonly form at low supersaturation with respect to calcite, grew by a spiral growth mechanism, with the attachment of ions at kink sites at atomic steps present on the calcite crystals (Frisia et al., 2000). Therefore, compact columnar calcite was interpreted as unlikely to be affected by diagenesis and the best archive of climate proxy data in speleothem-based research (Frisia et al., 2000).

Non-classical nucleation and growth theory, however, has shown the possibility that crystallization has multiple pathways: formation of pre-nucleation clusters, amorphous phases, nanocrystal aggregation, oriented self-assembly of nanocrystals into mesocrystals, crystallographic fusion of mesocrystals into single crystals, porous crystals, sponge crystals (Addadi et al., 2003; Navrotsky, 2004; Cölfen and Antonietti, 2005; Zhou and O'Brien, 2008; De Yoreo et al., 2015; Rodriguez-Blanco et al., 2015; Wolf and Grünewald, 2015; Jacob et al., 2017). In-situ experiments have also shown that non-conventional nucleation and growth mechanisms operate in caves (Demény et al., 2016). The implication of nucleation and growth including metastable phases, porous aggregates or porous single crystals on early diagenetic processes affecting speleothems is large.

The concept that many crystallization pathways are possible requires re-examination of speleothem nucleation and growth mechanisms, their influence in driving early diagenesis, and the impact of all depositional and post-depositional processes on the preservation of original chemical and physical properties. Defining early diagenesis in speleothem carbonates becomes problematic, because the transformation of possible transient products of crystallization into a stable carbonate could be considered already a post-depositional phenomenon. Although early diagenesis of speleothems usually occurs in the same environment where deposition took place (De Boever et al., 2017), it still has potential to influence carbonate geochemistry and a precise age determination by means of the U-series technique.

Radiometric dating of speleothems, if unaffected by post-depositional changes, allows deciphering Earth's climate evolution with unparalleled accuracy at least since the Permian (Hellstrom, 2006; Woodhead et al., 2006; Woodhead et al., 2012; Woodhead and Pickering, 2012). For decades, it was almost given for granted that stalagmites and stalagmitic flowstones were not prone to early diagenesis unless they consisted of aragonite. However, careful petrographic observations and trace element mapping revealed that even the thermodynamically stable low-Mg calcite can be affected by localized dissolution and re-precipitation (Bajo et al., 2016; Frisia, 1996; Frisia et al., 2002; Lachniet et al., 2012; Martín-García et al., 2009; Ortega et al., 2005; Railsback et al., 2002; Scholz et al., 2014). In Berner's conceptual framework, post depositional changes in speleothems should fall within the definition of early diagenesis, as these cave deposits rarely undergo burial. It is also known that transformations in stalagmites may occur within a few decades after deposition (Frisia et al., 2002; McMillan et al., 2005). Yet, whilst the analytical precision of U-series dating has been tremendously improved (Hellstrom, 2006), age inversions resulting from early diagenetic U-leaching, particularly when fabrics are initially porous (Frisia, 1996; Frisia et al., 2012; Genty et al., 2002) still deserve appropriate investigation. More so as it is now clear that caves host bacteria, archea and fungi, which may promote precipitation of precursor carbonates, and possibly influence dissolution and re-precipitation (Banerjee and Joshi, 2014; Banks et al., 2010; Bindschedler et al., 2010; Borsato et al., 2000; Busquets et al., 2014; Cacchio et al., 2004; Frisia et al., 2012; Jones, 2001, 2010; Keiner et al., 2013; Lavoie et al., 2010; Ortiz et al., 2014; Tisato et al., 2015). Speleothems, then, offer a most pertinent case study to investigate early diagenetic pathways in all carbonates, first because they can provide a time frame for the adjective early applied to diagenesis and, secondly, because their formation can be monitored from the initial stages of formation (Frisia et al., 2000; Tremaine and Froelich, 2013; Tremaine et al., 2011).

If cave carbonates are a perfect case study to investigate early stages of crystallization and transformations, dolomite rocks are exemplars of diagenesis in all its stages, including burial. Dolomite has a highly ordered crystal structure and ideal composition (50% mole Ca and 50% mole Mg), which results in sluggish growth kinetics at surface temperature. Kinetic barriers to dolomite formation have, in principle, led to the notion that most dolomite in the geologic record is diagenetic (Malone et al., 1996; Machel, 2004). Dolomite rarely forms in caves (Martín-Pérez et al., 2015), and it has been reported as a diagenetic product of huntite and hydromagnesite precursors (Sánchez-Román et al., 2011; Martín-Pérez et al., 2012). Even when cave waters may be supersaturated with respect to this mineral, stalagmites and flowstones still consist of calcite or aragonite (Bajo et al., 2016). The most likely explanation is the role of bio-mediation in the initial stages of dolomite precipitation, which has also been proposed for the origin of some peculiar types of speleothems (Vasconcelos et al., 2005; Aloisi et al., 2006; Baskar et al., 2006; Bontognali et al., 2008; Sánchez-Román et al., 2008; Bontognali et al., 2010; Kenward et al., 2013; Pacton et al., 2013; Bontognali et al., 2014; Bontognali et al., 2016). Yet, laboratory