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A novel concept in the growth and design of anhydrous carbonate minerals: nano-scale aggregation mechanisms

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ABSTRACT

A novel approach, designated as the particle-mediated, nano-scale, aggregation route, to the formation and growth of spherical and colloid-sized anhydrous carbonate mineral particles and hierarchically organized biomineral carbonate structures is discussed. This model is inconsistent with the conventional crystallization mechanism, which is primarily based on diffusion growth. It is determined by the initial formation of nanosized, crystalline particles, (singlets), and their subsequent aggregation into submicrometre and micron-sized carbonate particle assemblies. This concept is much more common in Nature than has previously been assumed. The number of new examples of its significance in the formation of inorganic and biogenic carbonate mineral solids has significantly increased in recent years. A few illustrations are presented to show the appearance of nanostructured and hierarchically organized carbonate particles formed through the nano-scale aggregation route in natural systems, together with those obtained from laboratory model experiments.

Keywords: aggregation, carbonates, mechanism of formation

1. INTRODUCTION

Anhydrous carbonate minerals are frequently found in Nature, commonly occurring as the main mineral constituents in rocks and sediments, and as the most common constituents of the bio-inorganic structures of the skeletons and tissues of many mineralizing organisms (TUCKER & WRIGHT, 1990; FLÜGEL, 2004; SONDI & JURAČIĆ, 2010; SONDI et al., 2011). Physico-chemical processes leading to the formation of anhydrous calcium carbonate polymorphs, i.e., vaterite, aragonite, and calcite, of different structures, sizes, morphologies, and surface properties, have been intensively investigated because of their importance in geo- and biosciences (ADDADI & WEINER, 1992; RICHTER et al., 1995; WANG et al., 1999; SONDI & JURAČIĆ, 2010). Most of the previously reported studies deal with the precipitation of calcium carbonate minerals in aqueous media through classical diffusion-type crystal growth (WESTIN & RASMUSON, 2005).

During the past decade, the formation of carbonate mineral particles exhibiting unusual structural, morphological and physical properties has been investigated in terms of their mineralogy, biology and chemistry (MELDRUM, 2003;

SONDI & SALOPEK-SONDI, 2005; MELDRUM & CÖLFEN, 2008; VIELZEUF et al., 2008). Lately, a new concept, the particle-mediated, non-classical crystallization process, in the formation of bio-inorganic, mesoscopically structured mesocrystals, was promoted (CÖLFEN & ANTONIETTI, 2005; NIEDEBERGER & CÖLFEN, 2006; WANG et al., 2006). These structures are composed of nanoparticle building blocks, and are characterized by a well-faceted appearance and anisotropic properties. This concept is much more common in biomineralization processes than has previously been assumed, and the number of new examples of the significance of mesocrystals in biomineral formation has significantly increased in recent years.

So far, only scant attention has been devoted to the formation of uniform and nearly spherical anhydrous carbonate particles, devoid of crystal habits and anisotropic properties, but still maintaining a crystal structure (SONDI & MATIJEVIĆ, 2003; SONDI & SALOPEK-SONDI, 2005; SONDI et al., 2008). The aim of this note is to discuss recent advances in the formation of well-defined and uniform nanostructured, colloidal carbonate particles, through the non-classical, inorganically and biologically induced nano-scale aggregation route and to identify some of the problems that still need to be addressed.

2. CASE REPORT AND DISCUSSION

The mechanisms of formation of unusual mineral structures and complex shapes have been a topic of discussion for decades. Morphological diversity and complexity of naturally occurring minerals in natural systems arises from the diferent physico-chemical mechanisms involved in their growth. The well-established, classical diffusion crystal-growth mechanism proposed by LAMER & DINEGAR (1950) suggests that colloidal mineral particles are formed when nuclei, coming from a short-lived burst, grow from the attachment of constituent solutes. During the past decade, further, unique, observations were presented including the formation of unusually uniform, spheroidal calcium carbonate particles of distinct crystallinity, despite the fact that they are aggregates of nanosized subunits (SONDI & MATIJEVIĆ, 2001; SONDI & SALOPEK-SONDI, 2005). The significance of the aggregation process in the formation of mineral particles from preformed nanocrystallites had already been observed in the late 1960s (PETRES et al., 1969). However, this disocvery has long remained neglected. Recently, it has been experimentally and theoretically established that many inorganic colloids, prepared by precipitation from homogeneous solutions, are composed of nanosized subunits (BAILEY et al., 1993; SONDI & MATIJEVIĆ, 2003; HE et al., 2004; LIU & ZHENG, 2004; ŠKAPIN & SONDI, 2005). Therefore, this mechanism was shown to be relatively common in the formation of colloidal particles with crystalline characteristics (PRIVMAN et al., 1999; NAVROTSKY, 2004; NIEDEBERGER & CÖLFEN, 2006).

Several important studies reported and discussed the formation of unusual structures based on a non-classical mechanism involving aggregation processes (SONDI & SALOPEK-SONDI, 2005; PRIVMAN et al., 1999; BAILEY et al., 1993), oriented aggregation assembly (PENN & BANFIELD, 1999; ALIVISATOS, 2000; BANFIELD et al., 2000), the development of an oriented architecture of bridged nanocrystals embedded in an organic matrix (OAKI et al., 2006) and the recently developed mesocrystal concept (CÖLFEN & ANTONIETTI, 2005; SONG & CÖLFEN, 2010). Comprehensive coverage of all these would be impractical here. Instead, a few basic examples are given concerning the aggregation mechanism involved in formation of nanostructured and colloidal mineral particles with remarkable morphological properties.

Firstly, consider the example of simple aggregation of carbonate colloid particles. Figure 1 displays a field-emission scanning electron microphotograph (FESEM) of unusual spherical and colloid-sized carbonate particles taken from

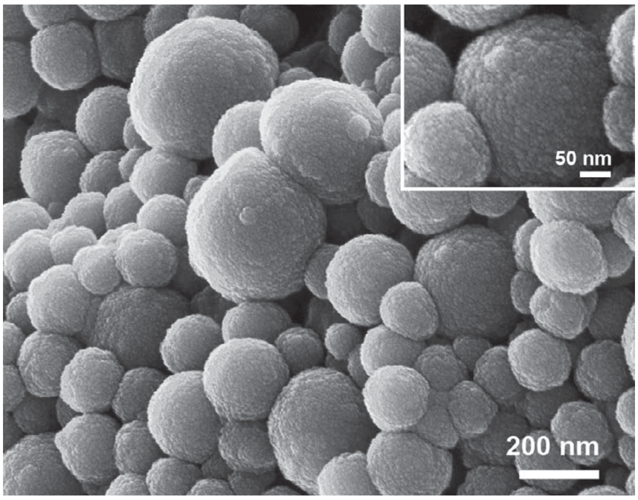

Figure 1: FESEM of spherical calcite particles composed of smaller nanosized units (the samples originate from the sediment of the freshwater lake of Jezero Kuti located on the Neretva River delta plain). Unpublished illustrations.

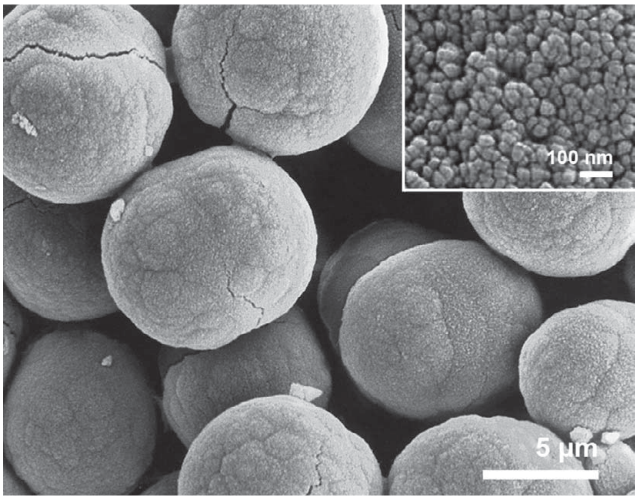

Figure 2: FESEM photomicrographs of spheroidal colloid-sized vaterite particles obtained by the enzyme-catalyzed decomposition of urea by urease in aqueous calcium salt solutions at room temperature. (Figure adapted from SONDI & SALOPEK-SONDI, 2005).

modern surface sediment of Kuti Lake, part of the deltaic system of the Neretva River, Croatia. At much higher magnification it is clear that these solids are composed of much smaller aggregated nanosized subunits (inset in Fig. 1). This implies that these solids did not follow the growth pattern through the classical crystallization pathways and diffusion growth, but rather were formed by the nonconventional aggregation of initially formed nanocrystallites. Analagous to this observation, Fig. 2 displays an FESEM photomicrograph of uniform and spherical colloid-sized vaterite particles obtained in the laboratory by the enzyme-catalyzed decomposition of urea using the urease enzyme in aqueous calcium salt solutions at room temperature (SONDI & SALOPEK-SONDI, 2005). Almost identical structures, (spherical colloid-sized vaterite particles, composed of much smaller nanosized singlets), were observed. Notably, the XRD peaks of the latter precipitate were significantly widened, additionally indicating that these spherical particles are composed of nanosize crystallites (Fig. 3). Applying the Debye-Scheerer equation, their size was estimated to be ~30 nm. In addition, SONDI & MATIJEVIĆ (2003) also demonstrated that uniform and spheroidal anhydrous carbonate particles from the aragonite group, witherite ($BaCO_3$) and strontianite ($SrCO_3$), generated through a biomimetic precipitation process, also consisted of nanosized subunits. Following these findings, aggregation processes at the nano-scale should be considered as an important mechanism in the formation of crystalline and colloidal carbonate mineral particles that are generated

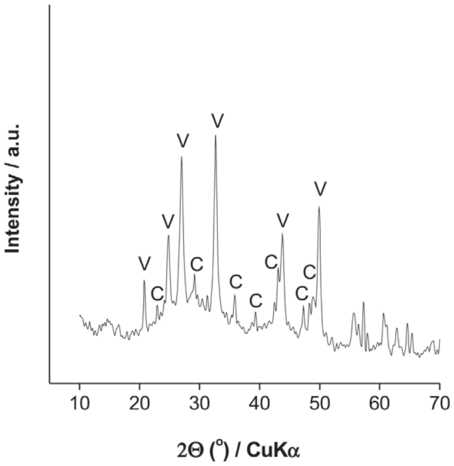

Figure 3: XRD pattern of vaterite (V) precipitate obtained by aging a solution containing 0.5 mol dm^{-3} urea, 0.2 mol dm^{-3} $CaCl_2$, and 0.5 mg cm^{-3} B. pasteurii urease at 25 °C for 2 min. (Figure adapted from SONDI & SALOPEK-SONDI, 2005).

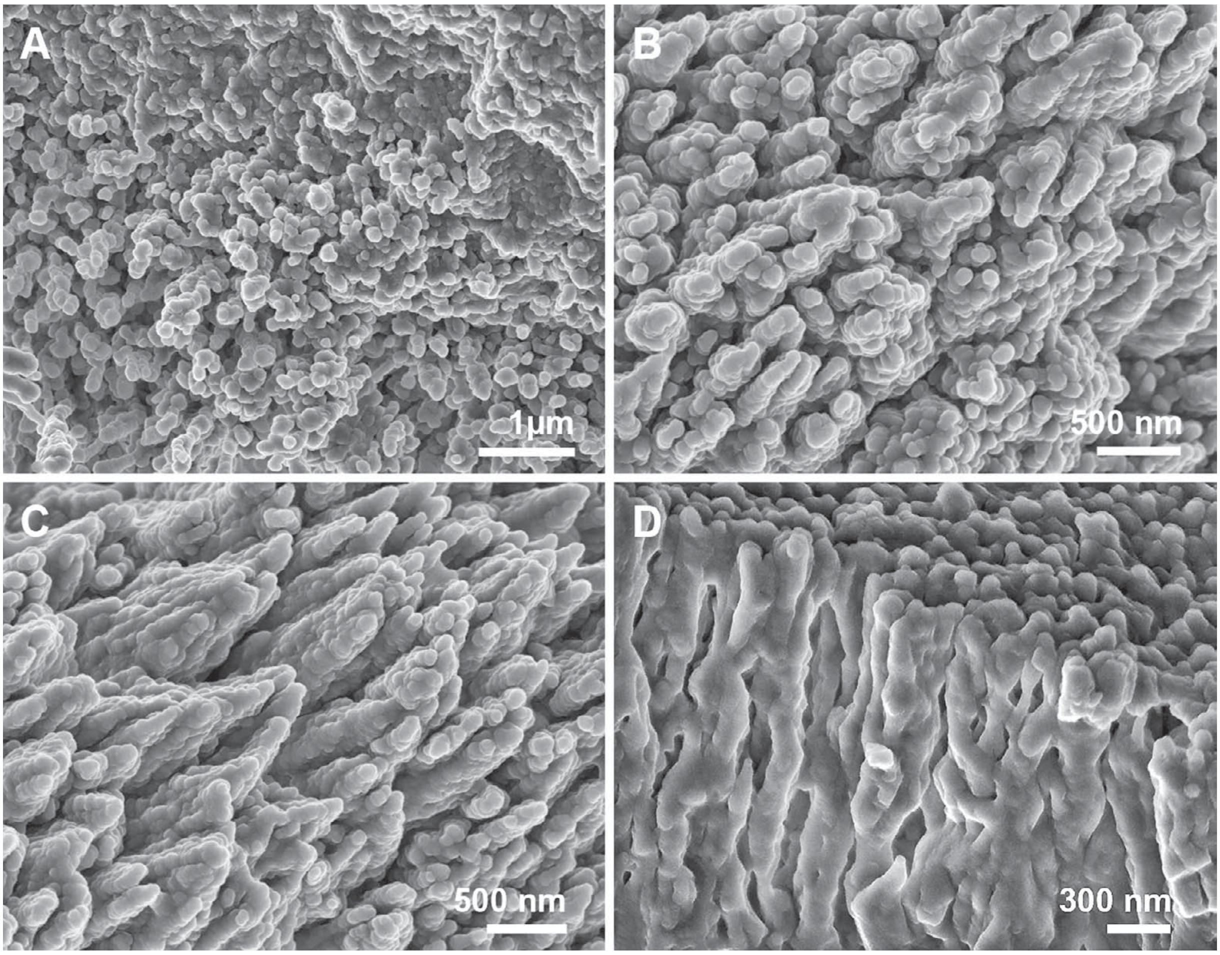

Figure 4: FESEM photomicrographs of different types of morphology on the native surface of a septal unit within the calyx: submicrometre-sized, nearly spherical crystallites (A), transitional forms of elongated cone structures built up of submicrometre-sized particles (B,C), and elongated aragonite fibres (D). (Figure adapted from SONDI et al., 2011).

in natural systems through complex biogeochemical processes, and through the laboratory model experiments under various experimental conditions.

Recently, several important studies have reported and discussed the fine-scale growth of unusual and hierarchically organized bio-inorganic aragonite structures involving a more complex, oriented nano-scale aggregation route (SETHMANN et al., 2007; VIELZEUF et al., 2008; SONDI et al. 2011). It was demonstrated that the internal crystal growth of aragonite fibres is governed by the aligned aggregation of preformed nanocrystallites and the subsequent coalescence processes that occur simultaneously. As an example, Fig. 4 demonstrates the essential principle of the matrix-mediated sequential growth of hierarchically organized fibrous aragonite structures in a skeleton of Mediterranean zooxanthellate scleractinian coral *Cladocora caespitosa* involving the nano-scale aggregation route (SONDI et al., 2011). It is based on an initial organic matrix-mediated formation of nanosized spherulites in the centres of calcification (Fig. 4A) and followed by the growth of aggregated and oriented cone-cluster assemblies, that are gradually built up of smaller nanosized units (Figs. 4B, C). What ensues is their subsequent morphological conversion through the coalescence of primarily formed nanoparticles and the formation of aligned fibrous units (Fig. 4D).

Figure 5 is an FESEM photomicrograph of unusual spheroidal aragonite particles of distinct crystallinity, which were aggregates of nanosized subunits obtained in the laboratory in an aqueous calcium salt solution containing urea and ethylene glycol at an elevated temperature of 160°C (ŠKAPIN & SONDI, 2010). Organization of the nanosized subunits of these aragonite particles closely resembles that of the fibrous aragonite in the skeleton of *C. caespitosa* shown in Fig. 4D. These findings confirm the hypothesis that the oriented aggregation is a common mechanism in the formation of naturally occurring and laboratory-obtained, hierarchically organized aragonite structures.

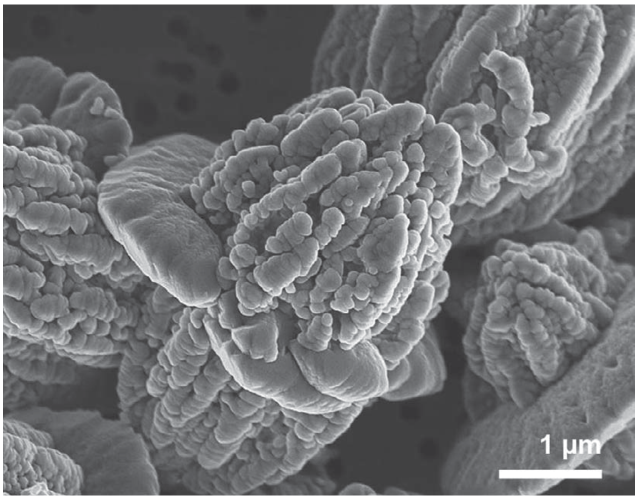

Figure 5: FESEM photomicrographs of aragonite obtained by ageing ethylene glycol solution containing 0.75 mol dm^{-3} urea, 0.25 mol dm^{-3} $CaCl_2$ at 160°C for 10 min. (Figure adapted from ŠKAPIN & SONDI, 2010).

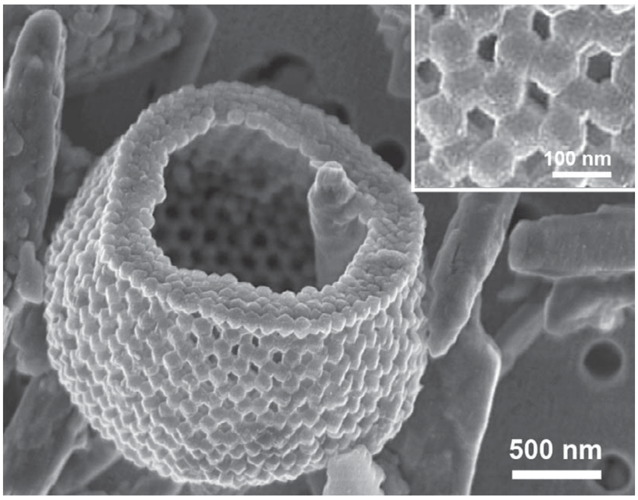

Figure 6: FESEM photomicrographs of heterotrophic protozoa showing the nanostructured shape of their lorica (the samples originate from the sediment of the marine lake of Malo Jezero on the island of Mljet, Adriatic Sea). (Figure adapted from SONDI & ŠKAPIN, 2010).

The appearance of nanostructured and hierarchically shaped bio-mineral structures in Nature is the rule rather than a chance event. Various organisms base the functionality of their structural components on the formation of nanostructured materials, functionally adapted to the living environment through the aggregation mechanisms. Figure 6 shows an example of the heterotrophic protozoa that build up their lorica from highly organized and nanostructured calcium carbonate solids (SONDI & ŠKAPIN, 2010).

As a final remark, the entire understanding of the role of the nano-scale aggregation processes in the formation of nanostructured colloidal carbonate minerals is still in its infancy. Further, more detailed and delicate investigations, focused on the formation of nanosized precursor phases and their mutual specific physico-chemical interactions at the initial stage of their formation, might clarify the mechanism of the entire precipitation process.

3. CONCLUSIONS

This note underscores the importance of nano-scale aggregation processes in the formation of biogenic and inorganic colloid-sized carbonate mineral particles. Understanding these mechanisms sheds light on the non-conventional formation of carbonate mineral phases in modern sediments, a situation commonly encountered in natural systems.

It needs to be pointed out that aggregation mechanisms are too complex to entirely determine the role of single processes of chemical and physical events involved in the formation of aggregated mineral solids in natural systems. It is clear that more focused and detailed investigations of substructured carbonate minerals from sedimentary systems, together with those obtained by model laboratory experiments could possibly contribute to the clarification of the mechanism of the aggregation processes encountered in bioinorganic and inorganic mineral structures in Nature.

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