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Nucleation and growth of Mg-bearing calcite in a shallow, calcareous lake

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ABSTRACT

Both inorganic and microbial processes play important roles in carbonate mineral precipitation in freshwater lakes. Identifying the individual factors that determine particle size, shape, composition, and the spatial relationships of carbonates with other constituents of the sediment are important for understanding sediment formation and nutrient cycling, and for providing input for lake management planning. We studied the formation of Mg-bearing calcite in Lake Balaton, a large, shallow, Mg-rich, calcareous lake in Hungary, by filtering particles from the water and analyzing them using X-ray powder diffraction and electron microscopy techniques. Mg-bearing calcite particles from Lake Balaton have distinct and remarkably consistent morphologies, independent of seasonal and annual variations in water temperature and composition. They are typically elongated parallel to the [001] crystallographic direction, are about 4 to 8 µm long, and even though appear to be composed of many smaller units, electron diffraction patterns indicate they are perfect single crystals. The Mg content of calcite increases from west to east, reflecting a gradient in lakewater composition. The calcite crystals are invariably attached to nm-scale flakes of smectite, suggesting that the clay mineral serves as a nucleation site. The templated nucleation may direct the growth of calcite parallel to the clay flakes, resulting in its elongated shape and single crystalline character. While in deep, oligotrophic lakes calcite typically nucleates on picoplankton cells, we rarely observe this phenomenon in Lake Balaton. Because of the shallowness of the lake, sediments are stirred up by even moderate winds and the movement of organisms, making nm-scale smectite flakes readily available for templating calcite nucleation. Thus, while calcite precipitation is an indirect consequence of biological activity (photosynthesis), the physical properties of the particles are primarily determined by inorganic factors.

1. Introduction

Calcium carbonate minerals are widespread on the surface of the Earth, can form both inorganically and by biological mediation, and are important in the global carbon cycle (Tucker and Wright, 2009); thus, they represent a crucial link between geology and life. Many aspects of the interplay between biology and the formation of inorganic carbonate crystals have been extensively studied, in both marine (Morse et al., 2007) and freshwater environments (Gierlowski-Kordesch, 2010). In this study, we focus on the precipitation of calcite in a shallow lake. In particular, we study the roles of microorganisms and pre-existing mineral particles in calcite nucleation, the effect of high dissolved Mg content on the composition and structure of calcite, and assess both biogenic and inorganic factors that affect the growth and, consequently, the size and shape of the precipitating crystals.

Biology can play multiple roles in the precipitation of carbonates in lacustrine settings, even in cases where the inorganic crystals are not used by the organism for a function (i.e., we are concerned here with biologically-induced rather than biologically-controlled carbonate mineralization). Firstly, photosynthesis by phytoplankton causes a shift in water chemistry that results in calcium carbonate supersaturation, triggering calcite precipitation (Thompson et al., 1997). Beyond changing the water chemistry, microorganisms can be key physical or chemical mediators of calcite

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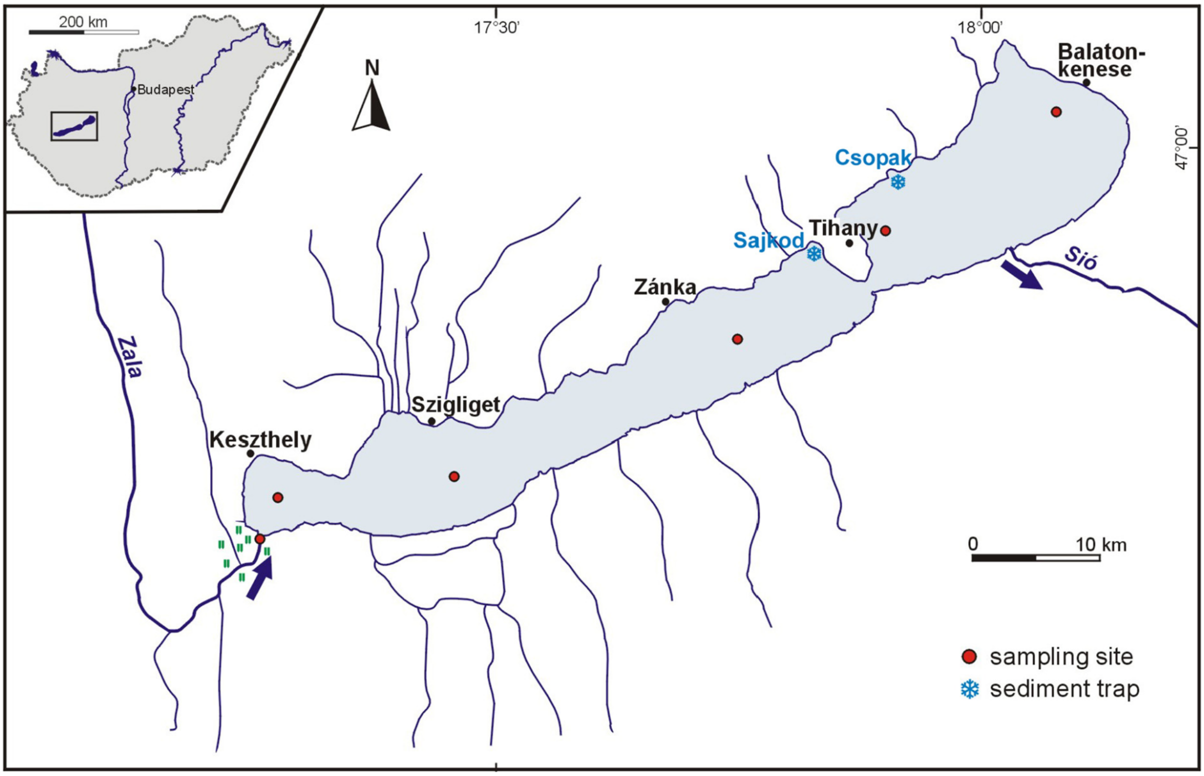

Fig. 1. Lake Balaton, with sampling sites marked where suspended particles were collected (red dots) and two sites where sediment traps were used in February 2012 and January 2017. The flow directions of the Zala river and the Sió canal, the major tributary and the only outflow of the lake, respectively, are also indicated. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

nucleation and also affect the growth of calcite seeds. Cyanobacteria provide suitable surfaces for the heterogeneous nucleation of calcite nuclei by binding Ca^{2+} on their surfaces, owing to the presence of extracellular polymeric substances (EPS) (Dittrich and Sibler, 2005; Obst et al., 2009; Schultze-Lam et al., 1996; Stabel, 1986; Zhang et al., 2015), and also affect the growth of the crystals (Benzerara et al., 2006). Seed formation may also be influenced by soluble metabolites that act as inhibitors or nucleation agents (Meldrum and Cölfen, 2008). In addition to the above processes that can be described by classical nucleation theory, calcite nucleation in biological systems often follows 'non-classical' pathways (De Yoreo et al., 2015). For example, the formation of prenucleation clusters in solution, or the deposition of amorphous calcium carbonate (ACC) as a precursor to calcite (Politi et al., 2008), as well as the formation of mesocrystals have been all described for calcite. Mesocrystals represent a special case of superstructure formation, since they are assembled from individual nanocrystals but scatter X-rays like a single crystal (Cölfen and Antonietti, 2005; Kim et al., 2014). Although several mechanisms of mesocrystal formation are known, in natural systems typically organic matrices or biopolymers are responsible for the oriented attachment of the nanoparticles (Bergström et al., 2015; Meldrum and Cölfen, 2008).

The effects of abiogenic controls over calcite nucleation and growth (including temperature, pH, alkalinity, Ca^{2+} and HCO_3^- concentrations) have been extensively studied (Morse et al., 2007; Niedermayr et al., 2013). Among the inorganic influences, the role of dissolved Mg is of particular interest for the present study. Mg is known to be an inhibitor of calcite nucleation, although the exact mechanism of its inhibitory effect remains unclear (Xu et al., 2013). Based on observations of natural systems (Richter et al., 2011), laboratory experiments (Davis et al., 2004; Hong et al., 2016) and atomistic simulations (Titiloye et al., 1993), Mg^{2+} can interact with specific crystal faces of calcite, resulting in a variety of distinct crystal morphologies (Fernandez-Diaz et al., 1996; Meldrum and Cölfen, 2008). Mg can also play a role in phase transformations of calcium carbonate: it was found to stabilize an initially precipitating, Mg-bearing ACC, and then facilitate its conversion to calcite (at Mg/Ca ratios relevant for the present study) (Purgstaller et al., 2016). Based on the amount of Mg incorporated into calcite, various terms are in use, including low-magnesium-calcite (LMC, with $<4\%$ $MgCO_3$), high-magnesium-calcite (HMC, with $>4\%$ $MgCO_3$), and very high-magnesium calcite (VHMC) or 'protodolomite' (Gaines, 1977), to refer to carbonate phases with near dolomite composition ($CaMg(CO_3)_2$) but a disordered arrangement of cations (Gregg et al., 2015; Zhang et al., 2010). In this study we discuss calcite particles with a $MgCO_3$ content ranging from 2 to ~30 mol%, and for these we use the term Mg-bearing calcite.

Several factors affecting calcite nucleation and growth can be studied in Lake Balaton, a lake of great cultural and economic (touristic) importance in landlocked Hungary. The lake has been a distinguished subject of scientific research for more than a century (Lóczy, 1913). For a surface area of ~600 km^2 the lake is extremely shallow (on average 3.5 m), resulting in the almost continual presence of sediment particles in the water column, stirred up by even relatively mild breezes. The lake has an elongated shape, with its long axis roughly along the W–E direction and is divided into Western and Eastern Basins by the Tihany Peninsula (Fig. 1). Due to the prevailing northerly wind direction, sand-sized particles are deposited along the south shore, whereas silt-sized particles dominate elsewhere in the sediment. Since most tributaries drain carbonate-rich terrain (Triassic limestone and dolomite in the north, young clastic sediments in the south), Balaton is a calcareous lake with a large dissolved Mg/Ca molar ratio, ranging from 1 to 4 (Tompa et al., 2014; Tullner, 2002). The main inflow, the Zala river enters the lake at its western end, while the only outflow, the Sió canal drains it near its eastern end, resulting in a west-to-east (W–E) chemical gradient in the lakewater composition (Müller and Wagner, 1978). Thus, Lake Balaton is a Mg-rich, calcareous, shallow lake with a W–E gradient in water composition and a N–S gradient in sediment particle sizes.

The water of Lake Balaton is supersaturated with respect to calcite within all extremes of physical and chemical conditions that have been recorded over the last century (Tompa et al., 2014) and probably through most of the ~12 thousand years of its history (Müller and Wagner, 1978). Although calcite forms at all times, the intensity and distribution of its precipitation is not uniform, since it is controlled primarily by temperature and the intensity of photosynthesis. About 40 to 80% of the bottom sediment consists of silt-sized calcite particles that precipitated within the lake, the rest being detrital particles (Cserny and Corrada, 1989; Müller and Wagner, 1978). Concerning the composition of the precipitating calcite, its Mg content is primarily determined by the dissolved Mg/Ca ratio of the water, which shows an increase from W to E along the main axis of the lake (Müller, 1970; Müller and Wagner, 1978; Tompa et al., 2014; Tullner and Cserny, 2003). In turn, since the Mg/Ca ratio is determined by the water budget of the lake, fluctuations in the water level affect the Mg content of the precipitating calcite, with dry periods resulting in higher concentrations of Mg both in water and in the solid precipitates (Müller and Wagner, 1978; Tullner, 2002). While buried in the sediment and in contact with Mg-rich porewater, calcite particles can be further enriched in Mg, a process that is thought to produce VHMC or 'protodolomite' in certain layers of the mud (Cserny et al., 1991; Müller, 1970; Müller and Wagner, 1978).

Although the physical properties of Mg-bearing calcite precipitating in Lake Balaton have not been studied in detail, several studies noted that the particles are typically a few µm large aggregates (Cserny et al., 1991; Müller and Wagner, 1978). The Mg-bearing calcite particles are within the size range that many indiscriminately filtering organisms, including several zooplankton species, filter through their bodies. Since a suspended, silt-sized carbonate particle load is almost always present in the lake, filtering organisms are exposed to a large inorganic particle burden, making them practically starve, even though a sufficient supply of organic material would be available (G.-Tóth, 1992). Thus, the physical properties of Mg-bearing calcite have some ecological effects that are transmitted along the entire food chain in the lake.

In this study we characterize Mg-bearing calcite particles that precipitate in Lake Balaton, and discuss their possible formation pathways. Given the interdisciplinary mineralogical/biological significance of Mg-bearing calcite in Lake Balaton, our main goal is to understand the major inorganic and biogenic factors that control the nucleation and specific properties of the particles that precipitate from the lakewater and that form most of the lake sediment.

2. Materials and methods

We studied Mg-bearing calcite particles collected from (1) suspended material that was filtered from lakewater, (2) sediment trap samples placed under the ice, and (3) material that precipitated from a water sample. (1) 40-l water samples were collected seasonally (in April and October, 2013, March and July, 2014, July and October, 2016, and March, 2017) at 5 locations along the longitudinal axis of the lake and in the mouth of the Zala river, by averaging a 3-m-long water column (Fig. 1 and Table S1). The particulate material was let to deposit, then the water was decanted and the remaining material filtered using 0.45-µm membrane filters, then dried at 40 °C. (2) Home-designed sediment traps were placed under the ice (with 40 to 100 cm water column above the collection vial), in order to avoid the resuspension of sediment by wind-driven turbulence and to collect the freshly precipitated material. Collection could be done for two- and three-week periods in February 2012 and January 2017, respectively, since the lake had no permanent ice cover in the four, unusually warm winters between 2012 and 2017. (3) In January 2016, we collected water from a hole in the thin ice, stored it for a week at ambient temperature (~5 °C), and studied the material that precipitated from it.

Water temperature, pH, electrical conductivity and oxygen saturation were measured at the time of samplings. Water samples were kept frozen until the concentrations of some dissolved species were analyzed using inductively-coupled plasma optical emission spectrometry (ICP-OES) or ion chromatography (IC) (for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}), and by titration (for HCO_3^{-} and Cl^{-}) (Table S2).

The mineralogical compositions of the particulate samples and the cell parameters of Mg-bearing calcite (the variations of which reflect the amount of Mg incorporation into the calcite structure) were analyzed using X-ray powder diffraction (XRD). XRD patterns were obtained with a Philips PW1710 instrument, using CuKα radiation, a graphite monochromator, and a step size of 0.035°. The procedure of interpreting XRD patterns was described in detail by Tompa et al. (2014).

The sizes, morphologies, microstructures and compositions of individual particles were observed using several microscopy techniques, including atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning TEM (STEM). For the AFM measurements, a drop of ethanol-diluted sample was placed on a mica plate. We used a PicoScan 2100 AFM for obtaining topography, deflection and friction images in contact mode. For SEM, we placed a drop of particle suspension onto an SEM pin stub covered by a conductive carbon tape. The samples were then either coated by a few-nm-thick Au/Pd layer for high-resolution imaging, or left uncoated for imaging at low accelerating voltages. Secondary electron (SE) images and energy-dispersive X-ray (EDS) spectra of the particles were obtained using a Philips XL30 environmental SEM with an attached EDAX X-ray detector at 25 kV accelerating voltage. Sediment trap samples were also analyzed using an FEI XL30-FEG SEM, operated at 30 kV accelerating voltage, and a JEOL 7600F SEM operated at 1 kV. For TEM analyses, particle suspensions were placed on Formvar and carbon-covered lacey TEM copper mesh grids. We obtained low-magnification bright-field images, selected-area electron diffraction (SAED) patterns and EDS spectra using a Philips CM20 TEM operated at 200 kV accelerating voltage and equipped with an attached Noran Voyager X-ray detector. For high-resolution TEM imaging (HRTEM) we used JEOL3010 and JEOL4000EX TEMs operated at 300 and 400 kV accelerating voltages, respectively. All three TEM instruments were equipped with a LaB_6 cathode. Additionally, samples embedded in epoxy and then thinned by Ar ion milling were studied at high resolution using a chromatic and spherical aberration-corrected FEI Titan PICO microscope, operated at a relatively low (80 kV) accelerating voltage in order to avoid beam damage. Chemical maps were measured using a probe aberration-corrected FEI Titan G2 80-200 STEM with a Super-X EDS system (both Titan instruments at the Ernst Ruska-Centre, Forschungszentrum Jülich, Germany).

3. Results

3.1. Particle size, morphology and structure

Typically, the fine-grained sediment of Lake Balaton is dominated by several µm-long, elongated Mg-bearing calcite particles, larger diatom fragments, and silicate minerals, most of which are clays (Fig. 2). In the following we focus on the properties of the Mg-bearing calcite particles.

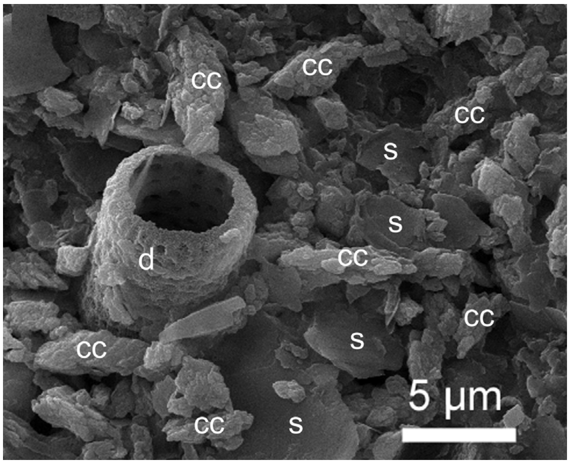

Fig. 2. Secondary electron SEM image of a sediment trap sample with Mg-bearing calcite particles (cc), diatom fragments (d) and clay minerals, most of which are likely smectite (s).

Both the sizes and morphologies of Mg-bearing calcite particles are distinct. The particles are typically about 2 µm wide and their length varies from about 4 to 8 µm, with an average around 5 µm (based on 44 particles). The particles characteristically appear to be aggregates of smaller (mostly between 100 and 300 nm) crystallites that either display distinct facets and angles consistent with the rhombohedral symmetry of calcite (Figs. 3a and S1) or have anhedral, rounded shapes (Figs. 3b and S2). According to AFM scans of ∼300 "bumps" on the surfaces of Mg-bearing calcite particles, their average lateral sizes and heights are 140–160 and ∼15 nm, respectively (Fig. S3). The basic appearance of the Mg-bearing calcite particles does not change noticeably with geographical location or between particles collected from suspended matter and from the sediment. Published images of Mg-bearing calcite particles collected from Lake Balaton in the 1970's and 1990's also look similar (Cserny et al., 1991; Müller and Wagner, 1978), suggesting that the morphologies displayed in Fig. 3 are typical for Mg-bearing calcite that precipitated from lakewater, and are independent of variations in temperature and fluctuations in the dissolved Mg/Ca ratio (Table S2).

We studied the structures of individual Mg-bearing calcite grains using TEM. The individual crystallites within the particles are discernible by their distinct outlines in amplitude-contrast images (Fig. 4a), and the sizes of the crystallites are in agreement with the SEM and AFM results. The particles show heterogeneous contrast in TEM bright-field images, with a change from the thinner edges to the centers of the particles, as a result of particle thickness variations. SAED patterns recorded from entire aggregates show a single set of sharp reflections, suggesting that the

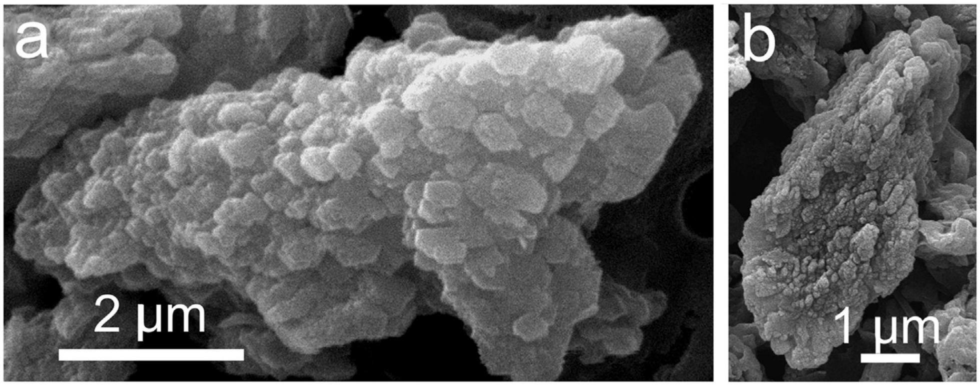

Fig. 3. Secondary electron SEM images of typical Mg-bearing calcite particles that appear to consist of either (a) euhedral or (b) irregularly-shaped nanocrystals.

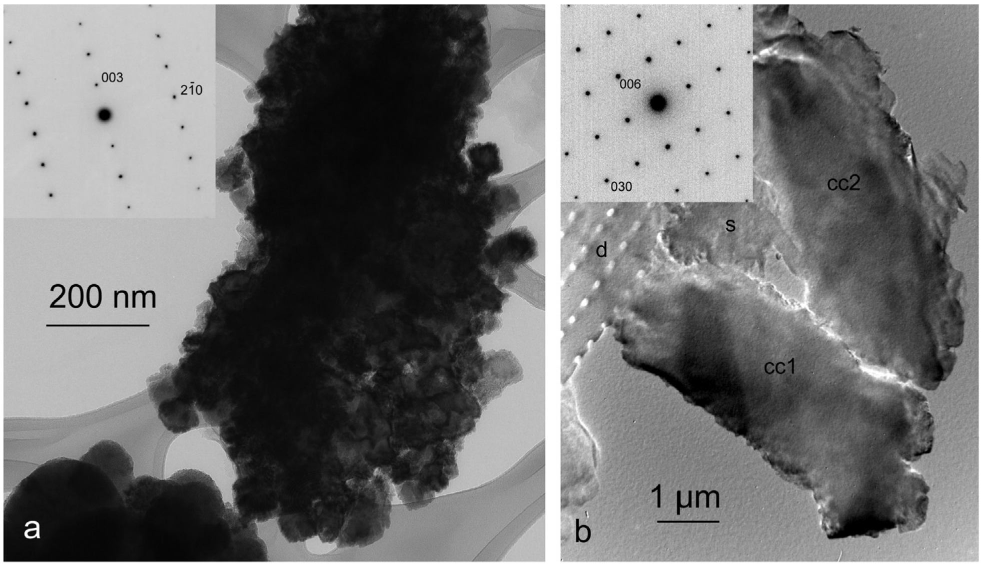

Fig. 4. (a) Bright-field TEM image and corresponding SAED pattern recorded from a typical Mg-bearing calcite particle, with [100] parallel to the electron beam direction, suggesting a single crystalline character of the entire particle. (b) Bright-field TEM image of two Mg-bearing calcite grains (cc1 and cc2), both of which are single crystals (the inserted SAED pattern corresponds to cc1), attached to smectite (s) and a diatom fragment (d).

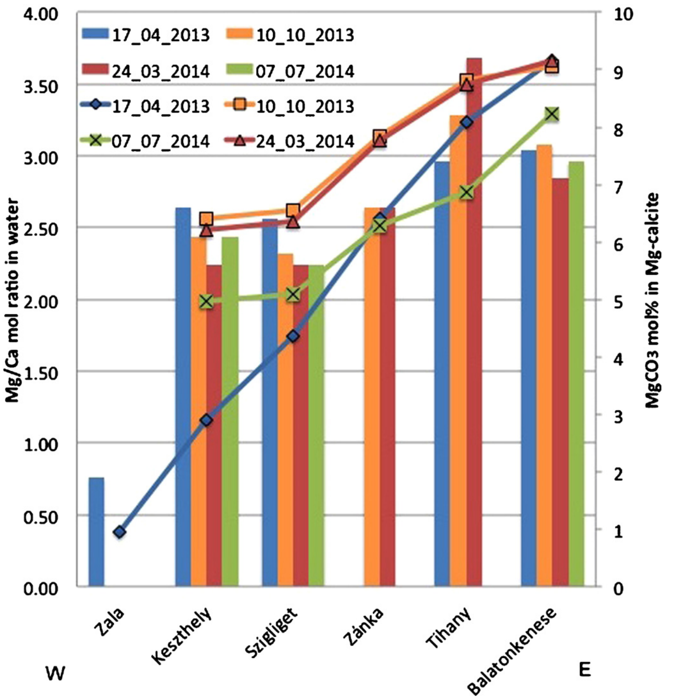

Fig. 5. Mg/Ca mol ratio measured in water (marked lines) and $MgCO_3$ mol% of Mg-bearing calcite in filtered, bulk suspended material (columns), as determined from XRD analysis, arranged according to geographic location from west to east (left to right). The sample "Zala" represents material obtained from the Zala river, the main inflow of the lake, whereas the other five sampling sites are located along the central, W–E axis of the lake (see Fig. 1).

Mg-bearing calcite particles are in fact single crystals. Thus, even though the particles appear to be composed of many distinct crystallites, their apparent subunits share the same crystallographic orientation. In addition, the elongation axis of most particles is parallel to [001] (Figs. 4b and S4), suggesting that some distinct mechanism controls the nucleation and growth of the particles.

3.2. Particle compositions

In a previous study (Tompa et al., 2014) we analyzed sediment cores and showed that the Mg content of Mg-bearing calcite increases from west to east along the long axis of the lake, in parallel with an increasing dissolved Mg/Ca ratio in the lakewater. Here, we present the compositions of Mg-bearing calcite particles that were filtered from the water, and thus better represent freshly precipitated material than the sediment particles. Bulk compositions of suspended Mg-bearing calcite particles were obtained by measuring the shift of the calcite 104 peak in X-ray powder diffractograms, with the zero point of the spectrum calibrated on the basis of the quartz 011 peak (details of the methodology were described by Tompa et al., 2014). The $MgCO_3$ mol% of Mg-bearing calcite varied between 6.1 and 8.2% at different locations (Fig. 5 and Table S3). The distribution of compositions shows a slight increase of the Mg content from west to east, similar to the trend observed in sediment cores, independent of the season. Samples from Tihany and Balatonkenese, located in the Eastern Basin of the lake, have the largest Mg contents. At three of the four sampling dates the increase in the Mg content of calcite from west to east follows approximately the same trend as the dissolved Mg/Ca mol ratio in the water. The water chemistry was special on April 17, 2013, as the Zala river, the main tributary of Lake Balaton, was flooding, resulting in a steeper than usual rise of the Mg/Ca ratio towards the east.

The Mg contents of individual calcite grains were studied using EDS in the TEM. From the filtered material that was collected at four locations (Keszthely, Szigliget, Tihany and Balatonkenese, see Fig. 1), a total of 44 particles were analyzed (with a low electron dose, and each spectrum acquired for 60 s). The compositions scattered significantly, with the $MgCO_3$ content of calcite ranging from 2 (Keszthely) to as high as 15 mol% (Tihany) (Fig. S5). However, the average of all individual-particle analyses was 6.8%, which is consistent with the data derived from the XRD analysis of bulk samples. The averages of measured compositions at each of the five locations did not differ from one another significantly, probably due to the relatively small number of analyzed particles.

The partially ordered distribution of Mg within the calcite structure was shown in the past to result in characteristic features in SAED patterns (Reeder, 1992; Wenk et al., 1983). However, we could observe neither supercell reflections, nor continuous intensity in SAED patterns that could be interpreted as resulting from structural changes due to Mg ordering. All SAED patterns obtained from Mg-calcite particles from Lake Balaton were consistent with calcite, suggesting a disordered arrangement of Mg ions in the structure. We note that dolomite is also present as a minor phase in both filtered and sediment material, and its possible origins will be discussed in a future study.

3.3. Association of Mg-bearing calcite with smectite

Several studies found that calcite tends to nucleate on the surfaces of picoplankton cells in freshwater lakes (e.g., Dittrich and Obst, 2004; Stabel, 1986; Thompson et al., 1997). The positions of decomposed cells were visible in electron micrographs as holes in the carbonate mineral (Obst et al., 2006). In order to examine whether biological surfaces provided nucleation sites for calcite crystallization in Lake Balaton, we ion-milled thin TEM specimens from the Mg-bearing calcite powder that was filtered from lakewater collected near Balatonkenese, in the Eastern Basin (see Fig. 1); however, no cells could be observed inside the calcite grains. Instead, Mg-bearing calcite grains were typically attached to or enveloped by nanometer-scale, disordered, wavy packets of layer silicates (Figs. 6, S6, S7, and S8). We identified these layer silicates as smectite on the basis of their compositions, highly disordered structures, very small grain size, and the measured spacings between basal planes (ranging from about 10 to as large as 24 Å, Figs. 6c, 6d and S8). The origin of smectite could be either detrital or authigenic. The formation of layer silicates was observed in calcareous lakes (Zeyen et al., 2015). However, smectite group minerals are the dominant layer silicate constituents of solid material that is delivered into the lake by streams (Weisz et al., 2000), so we think the majority of smectite is allochtonous. Even though other detrital minerals such as quartz and feldspars also occur in the suspended particle load, their grains were not observed to be aggregated with Mg-bearing calcite.

Although an exact orientational relationship between Mg-bearing calcite and smectite could not be established, it appears that smectite flakes are attached to the (104) or (110)-type faces of the calcite particles. The attachment of smectite flakes to the surfaces of Mg-bearing calcite is a characteristic feature for suspended matter in Lake Balaton, under conditions that are typical for most of the year. In such typical samples we did not observe any picoplankton cells or other biological objects inside the Mg-bearing calcite crystals.

3.4. Association of Mg-bearing calcite with microorganisms

We studied the features of Mg-bearing calcite that precipitated from a water sample that was collected from a hole in the ice in January 2016. This sample proved to be free of clay minerals, and

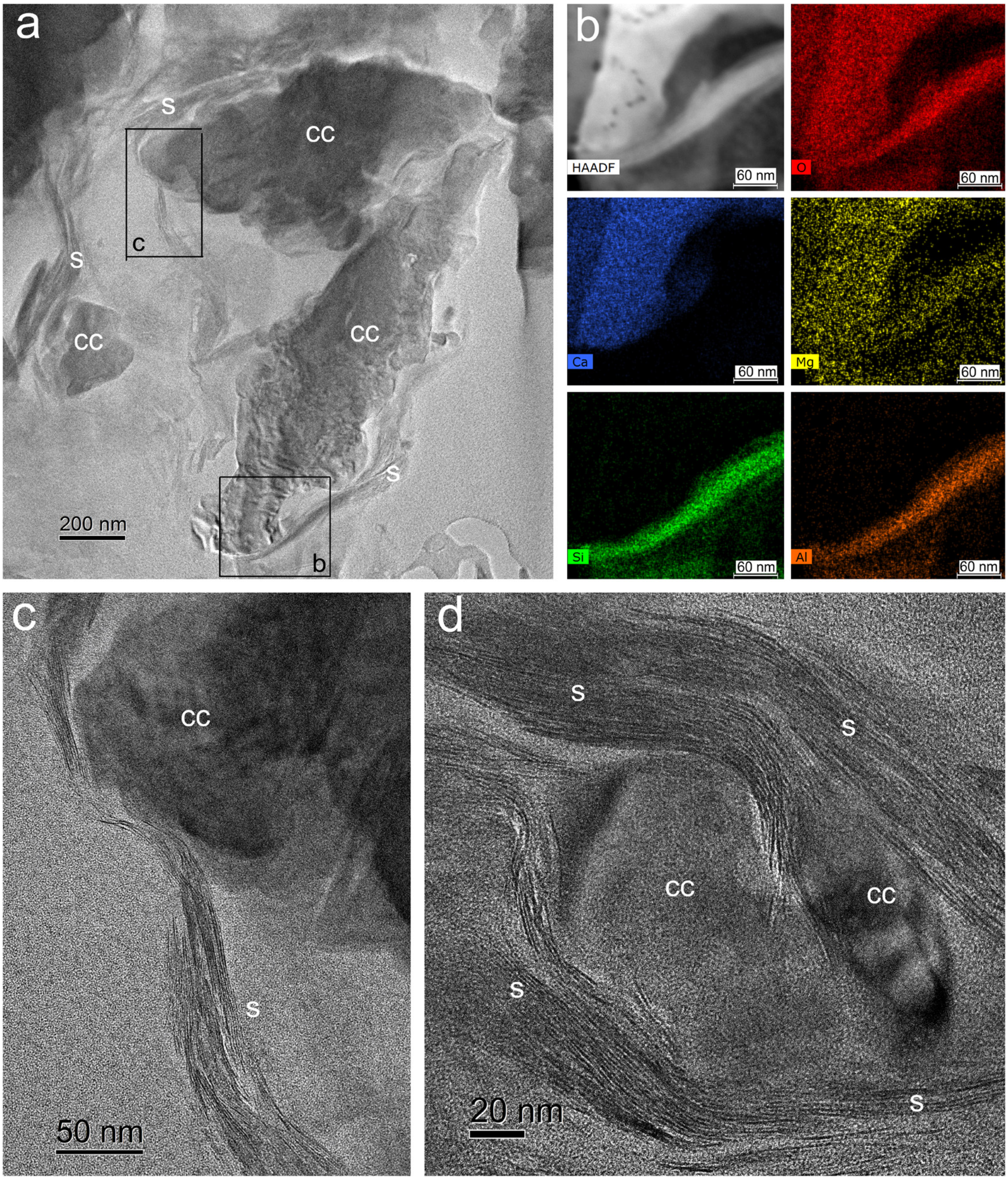

Fig. 6. Association of Mg-bearing calcite with smectite in an ion-milled sample prepared from suspended particles. (a) Low-magnification TEM image of Mg-bearing calcite grains (cc) with smectite flakes (s) attached to their surfaces. (b) High-angle annular dark-field (HAADF) STEM image and corresponding EDS elemental maps of Mg-bearing calcite and smectite, obtained from the boxed area in (a), as indicated by "b". Smectite contains O, Si, Al and Mg, whereas calcite contains Ca and minor Mg. (c) HRTEM image of the upper boxed area in (a), showing smectite attached to calcite. (d) HRTEM image of two Mg-bearing calcite grains, embedded in wavy packets of smectite layers.

the properties of Mg-bearing calcite particles were distinct from the typical particles that were described above. Instead of being attached to smectite, Mg-bearing calcite appeared to encrust the cells of microorganisms (which were identified as biological objects both by their morphologies and C- and P-rich compositions) (Fig. 7a). Mg-bearing calcite particles formed porous tubes several µm long and about 1 µm wide (Figs. 7b and c), the peculiar morphology probably being governed by the elongated shapes of the cells that the calcite encrusted. Some of the tubes had significantly higher Mg content (up to 30% $MgCO_3$) than the "ordinary" Mg-bearing calcite particles described above, as analyzed using EDS in the TEM. Since similar microbe/calcite associations were never observed in samples obtained from the sediment or the filtered suspended matter, we consider the occurrence of tube-shaped Mg-bearing calcite particles highly unusual for Lake Balaton.

4. Discussion

The observed features of Mg-bearing calcite from Lake Balaton provide interesting insights into and raise further questions about the nucleation and growth of carbonates in freshwater environments. Some of the special features of the lake, including its high dissolved Mg/Ca ratio and shallowness affect the properties of the carbonates that precipitate from the water.

The intimate and specific association of Mg-bearing calcite with smectite raises the question whether the two minerals came into contact by coagulation in the water or the clay mineral served as

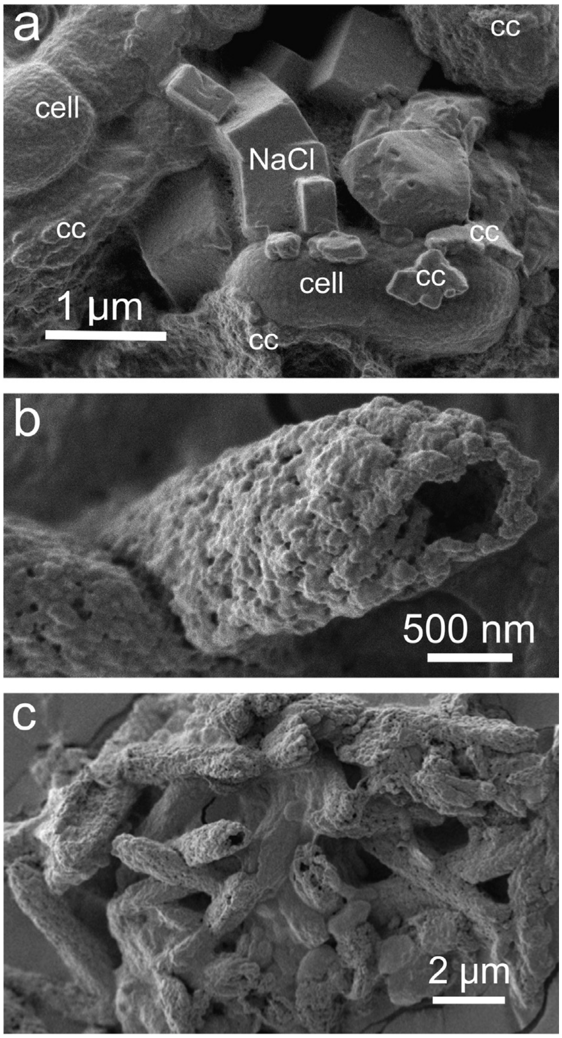

Fig. 7. Secondary electron SEM images of unusual Mg-bearing calcite particles. (a) Calcite (cc) on the surfaces of cells of an unidentified microorganism (cell). (b and c) Tube-shaped Mg-bearing calcite, probably formed by the encrustation of microorganisms similar to those in (a).

a heterogeneous nucleation surface for Mg-bearing calcite. Based on the prevalence of smectite/calcite associations in the studied samples, and in agreement with literature evidence for the role of layer silicates in enhancing the nucleation of Mg-bearing carbonates (Cuadros et al., 2016; Díaz-Hernández et al., 2013; Xu et al., 2018), we assume that the clay minerals provide favorable surfaces for the formation of Mg-bearing calcite nuclei.

Carbonates provide many examples for non-classical pathways of crystal nucleation (De Yoreo et al., 2013), including the formation of prenucleation clusters or solid precursors that either form in compartmentalized spaces or become anchored to heterogeneous surfaces. Clay minerals of the smectite group are expandable three-layer (TOT) silicates that are known to create periodic structures in water with extremely long (tens of nm) distances between adjacent TOT structural units (Gilbert et al., 2015). Images such as the ones shown in Figs. 6, S8 and S9 suggest that the smectite mineral in Lake Balaton could provide both a compartmentalized space and a suitable surface for Mg-bearing calcite nucleation.

In addition, smectites have a deficit of positive charge in the interlayer space, which results in the preferential diffusion of dissolved cations into the interlayer space. The enrichment of Ca^{2+} and Mg^{2+} ions near or between the layers of smectite relative to the bulk of the solution results in locally high supersaturation at the smectite/water interface, triggering the nucleation of calcite. In a study of the effects of suspended mineral particles on calcium carbonate nucleation, montmorillonite was found to cause instantaneous precipitation of calcite, whereas in the presence of quartz and kaolinite vaterite precipitated at much higher supersaturations (Kralj and Vdović, 2000). Thus, calcite precipitation on smectite is favored if the clay mineral is available. Similarly, the templated nucleation of calcite was described on the (001) surface of mica (Xu et al., 2018); however, in contrast to the mica/calcite intergrowths, preferred orientational relationships between smectite and calcite associations in Lake Balaton were not observed (Fig. S10).

The sediments of the shallow lake are stirred up by even mild breezes, resulting in the almost continual presence of submicrometer-sized smectite flakes in the suspended particle load. Even the sediment traps that were placed under the ice contained Mg-bearing calcite with attached smectite. Presumably the motion of organisms (including Copepods that were found in large numbers in the traps) provided enough turbulence to result in the suspension of submicrometer smectite flakes. We interpret the distinct and relatively uniform sizes and shapes of Mg-bearing calcite particles as resulting from their nucleation on smectite. A peculiar consequence of the inorganically constrained size (and perhaps shape) of Mg-bearing calcite particles is that some zooplankton species have to filter them through their bodies, along with their food supply (G.-Tóth, 1992; G.-Tóth and Zánkai, 1985), creating a stressed environment for these organisms.

The sample that was precipitated from water collected from the ice-covered lake (Fig. 7) is unique both in terms of the absence of clay minerals and the properties of the Mg-bearing calcite grains in it. This sample probably represents highly unusual conditions in the lake, when clay surfaces were not available, and calcite nucleated on microorganisms. The sizes and morphologies of the observed cells suggest they are picoeukaryotes (green algae producing oil droplets) which were described as the dominant form of phytoplankton in Lake Balaton during winter, irrespective of whether the lake is frozen (Vörös et al., 2009).

The Mg content of calcite may be a consequence of the way it nucleated. The typical, smectite-associated Mg-bearing calcite particles contain variable but less than 15% $MgCO_3$, whereas the particles that encrust microorganisms may contain as much as 30% $MgCO_3$. It has been widely discussed that the Mg content of "biogenic" calcite can be higher than the concentration that represents equilibrium between the solid phase and the solution (Morse et al., 2007), and extracellular polymers can strongly affect Mg incorporation (Zhang et al., 2015). On the other hand, the bulk composition of smectite-associated Mg-bearing calcite is primarily determined by the Mg/Ca ratio in lakewater (Fig. 4), although the large variation between the Mg contents of individual particles is unclear (Fig. S5). Mg incorporation into calcite was shown to affect crystal morphology as well, producing elongated particles by Mg ions causing step rounding and surface segmentation (surface roughness) (Davis et al., 2004; Hong et al., 2016). Although the particles observed in this study are also elongated, their morphologies are unlikely to be related to the Mg content, since all particles have similar shapes, independent of their compositional differences. It should be noted that the Mg concentration is just one of several variables that can affect the morphology of the precipitating calcite (Meldrum and Cölfen, 2008). The presence of dissolved organic compounds can have a particularly strong influence on morphology; however, we have no information on the specific organic constituents in the lakewater.

Based on their distinct, aggregate-looking morphologies, the Mg-bearing calcite particles could be interpreted as mesocrystals that formed by the oriented attachment of smaller building blocks (Cölfen and Antonietti, 2005; Kim et al., 2014). Small misalignments would be probably inevitable if the individual blocks had been crystalline when they attached; however, SAED patterns suggest that the Mg-bearing calcite particles are perfect single crystals. We assume that the smectite surface templates the development of the calcite single crystals. By using cryo-TEM to study templated calcite nucleation on an organic surface, Pouget et al. (2009) showed that initially prenucleation clusters form in the solution that aggregate into ACC particles on the organic surface. Then nanocrystalline domains form within the amorphous particles, with the template stabilizing a single orientation into which all merging particles convert. Even though the formation of ACC in Lake Balaton is unlikely because of a relatively low saturation index (log Q/K ranging from about 1 to 2 with respect to calcite), a similar scenario seems likely for the formation of mesocrystalline-like Mg-bearing calcite particles. The growth of the initial crystal nuclei could have been guided by the orientation of the smectite surface on which they formed, resulting in a single crystallographic orientation, once all component grains of the particle have merged. Thus, the smectite flakes in Lake Balaton both enhance Mg-bearing calcite nucleation and direct its growth, resulting in particles with characteristic sizes and morphologies. Interestingly, the constrained physical properties of the precipitating calcite affect the ecology of the lake, since the few µm-sized particles create an immense ballast for passively filtering organisms, to the effect of limiting their biomass (G.-Tóth, 1992), and causing a cascading effect up the aquatic food chain.

5. Conclusions

Mg-bearing calcite formation in shallow Lake Balaton results from an interplay of biogenic and abiogenic factors. Calcite precipitation is an indirect consequence of photosynthesis, but the physical dimensions of calcite particles are governed by inorganic factors. Both the sizes and the shapes of the calcite particles appear to be controlled by the fact that they nucleate on smectite flakes, which are practically omnipresent in the lake as a result of its shallowness. While the high dissolved Mg concentration originates from the geology of the catchment area, algal photosynthesis is primarily responsible for the increasing Mg/Ca ratio from W to E (by removing significantly more Ca^{2+} than Mg^{2+} from the water through calcite precipitation), resulting in an increasing Mg content in the precipitating calcite particles. The phenomena controlling the physical properties and compositions of precipitating calcite are probably not unique to Lake Balaton. In particular, the nucleation of calcite on smectite clays is likely to occur in similar, shallow-water environments and in soils. The significance of this process both at present and in the geological past is yet to be assessed.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2018.05.029.

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