Final Report
on OTKA project K116732 entitled

“Karbonátásványok képződése a Balatonban”
“Formation of carbonate minerals in Lake Balaton”

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Aims

The primary aim of this project was to understand the formation of carbonate minerals in Lake Balaton. In particular, we wished to

(1) establish the roles of biogenic and inorganic factors in the formation of Mg-bearing calcite, the main mineral phase that precipitates from lakewater;

(2) to characterize the physcal and chemical properties of anomalous dolomite and to determine whether it forms contemporaneously; and

(3) to use the information obtained in (1) and (2) to assess the current magnitude, character and ecological significance of carbonate deposition in Lake Balaton.

The original scope of the research has been significantly expanded. As we progressed along the planned lines of study, new problems and new collaborations arose that were related to the original goals and judged to be significant enough to include in our research project. Among these, we

(4) studied carbonate biominerals (mussels and otoliths) from the lake;

(5) characterized Mg-rich carbonates in a lake sediment core from 5500 and 8100 years ago;

(6) performed structural studies on protodolomite from Lake Fertő.

Topics 4, 5 and 6 are still ongoing projects, some of which resulted in new research proposals.

Below we will briefly summarize our results according to the above six topics.

Results

1. Precipitation of Mg-bearing calcite

Mg-bearing calcite has been known since the 1970's as the major phase of the lake sediment, and its precipitation from lakewater was also recognized (Müller and Wagner, 1978; Cserny, 2002). However, our studies shed new light onto the details of its formation and its significance in the lake ecosystem.

1.1 Observation of Mg-bearing calcite formation in Lake Balaton

From our analyses of suspended matter and sediment trap samples we found that Mg-bearing calcite precipitates from the water of Lake Balaton in all seasons. The calcite grains have distinct sizes, morphologies (5 to 8 µm long, about 2 µm wide), compositions (from about 2 to 14% $MgCO_3$ content, with the Mg content increasing from West to East, parallel to the changes in water chemistry), and are always associated with nm-scale flakes of smectite clays (Fig. 1). We attributed the distinct properties of the calcite to the fact that it nucleates on the clay surfaces - the templated nucleation of calcite on clays might be a special feature of Lake Balaton, since the clays are present in the suspended matter most of the time as a result of wind-driven turbulence of the shallow lake.

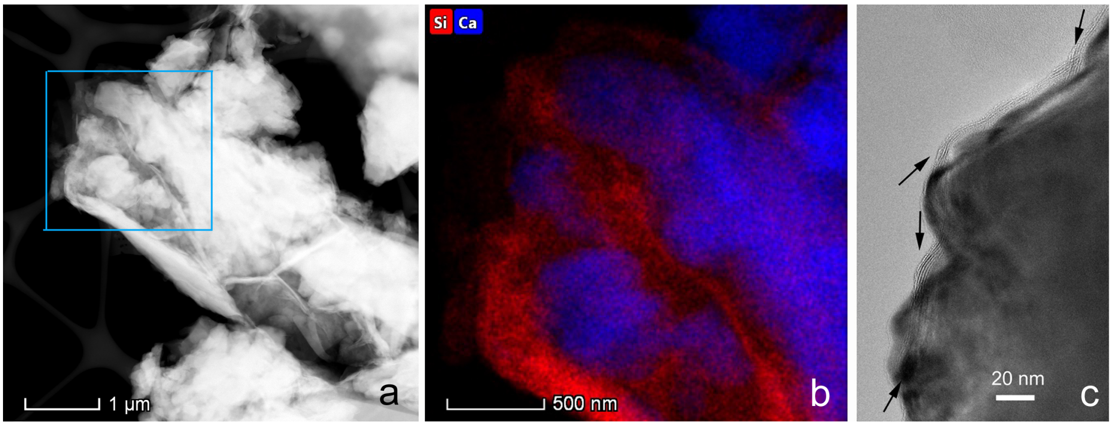

Fig. 1. TEM analysis of Mg-bearing calcite and attached flakes of smectite. (a) STEM HAADF image, (b) element maps of Ca and Si in the boxed area in (a), and (c) HRTEM image of calcite with a few-layer-thick smectite flake on its surface.

An interesting observation from the winter sediment trap samples is that even when the lake is covered by ice, the movement of invertebrates (mostly small Crustaceans) stirs up the sediment to suspend smectite flakes in the water and make them available for heterogeneous Mg-calcite nucleation. Another important point is that the specific size range of the Mg-calcite particles (owing to the formation process on smectite) causes a strain on passively filtering planktonic crustaceans that are key species in the food pyramid in the lake.

The observed calcite-smectite associations were described and the implications of the potential heterogeneous nucleation of calcite on smectite were discussed in a paper published in EPSL (a D1 category earth sciences journal):

Nyirő-Kósa, I., Rostási, Á., Bereczk-Tompa, É., Cora, I., Koblar, M., Kovács, A., Pósfai, M. (2018) Nucleation and growth of Mg-bearing calcite in a shallow, calcareous lake**. Earth and Planetary Science Letters**, 496, 20-28.

1.2 Molecular dynamics simulations of the heterogeneous nucleation of calcite

Since the observations discussed under 1.1 suggested that calcite nuclated heterogeneously on smectite, we wished to understand the atomic-scale details of this process. We performed MD simulations of the formation of ion associations (clusters) in aqueous, carbonate-bearing solutions between layers of clay minerals (montmorillonite and kaolinite). Ionic "prenucleation" clusters (Gebauer et al., 2018) were found to form preferentially in the interlayer solution instead of on the clay surfaces; later the clusters tended to be anchored to the clay (Fig. 2). Montmorillonite (a member of the smectite group) was far more efficient in capturing clusters from solution than kaolinite, confirming that the associations of smectite with calcite indeed could have resulted from the heterogeneous nucleation of calcite on the clay surface. The calculations also suggested that the presence of Na^+ has an inhibitory effect on cluster adsorption on the clay; thus, while in freshwater systems the localization of prenucleation clusters on clay surfaces promotes the nucleation of calcium-magnesium carbonate minerals, it is probably less efficient in seawater.

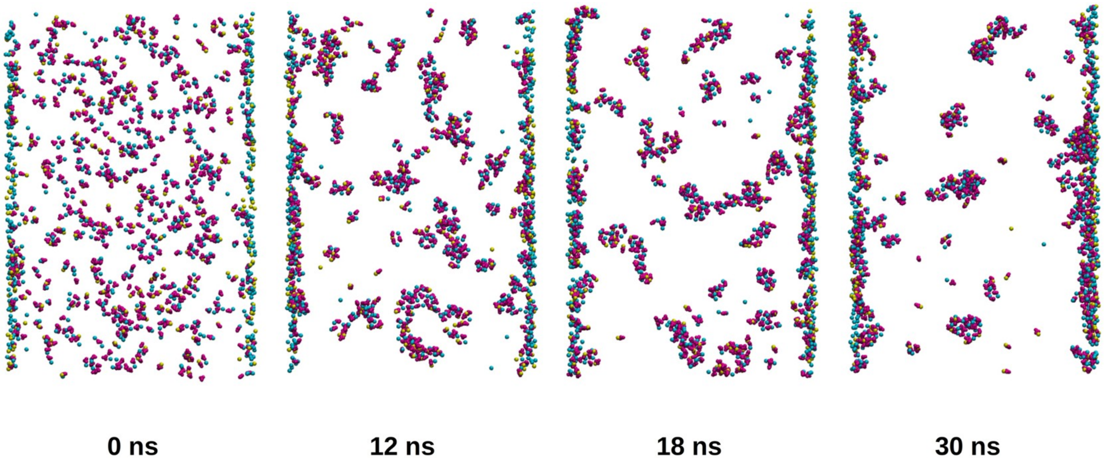

Fig. 2. Snapshots of the formation and attachment in ionic clusters in a solution between two montmorillonite layers, simulated over a total of 30 ns.

The results of the MD smulation were published in Chemical Geology (D1 in geochemistry):

Fodor, M.,Ható, Z., Kristóf, T., Pósfai, M. (2020) The role of clay surfaces in the heterogeneous nucleation of calcite: molecular dynamics simulations of cluster formation. **Chemical Geology**, 538, 119497.

1.3 Laboratory experiments of calcite precipitation

In order to quantitatively characterize the enhancement in calcite formation by the heterogeneous nucleation mechanism on smectite, we performed laboratory precipitation experiments, by using an automatic titrator. A carbonate buffer was titrated with Ca- (and Mg)-bearing solutions, both in the absence and presence of smectite. During the titration the free Ca^{2+} concentration was monitored using an ion selective electrode. The point of nucleation could be identified by a sudden drop in Ca^{2+} activity (LaMer curve; Gebauer at al. (2018), see Fig. 3).

Comparing the curves obtained in different experiments, we found that calcite nucleation took place at much lower supersaturation (at a smaller amount of dosed solution) than in the homogeneous solution. However, when Mg was also present in the solution (at a Mg:Ca ratio of 4:1), there was no significant difference in the point of nuclation (Fig. 3).

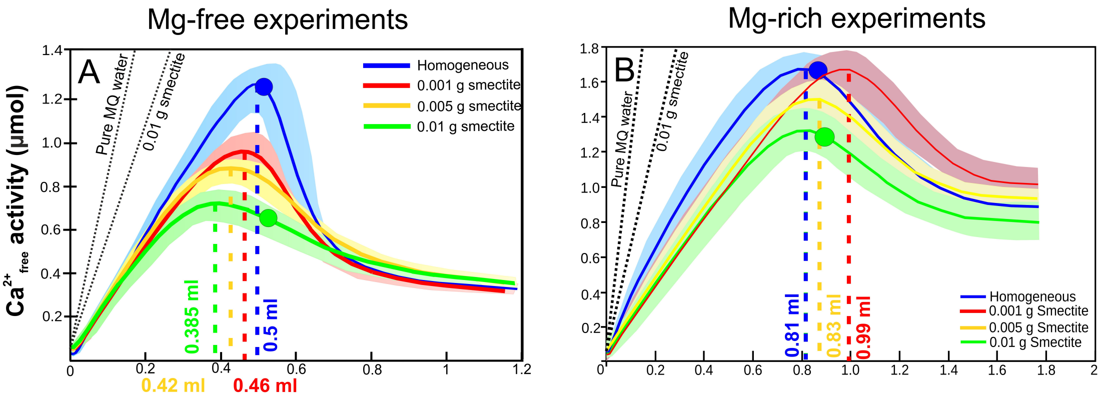

Fig. 3. Results of titration experiments designed to precipitate carbonates, both in the absence and presence of smectite. The measured activity of Ca^{2+} is shown as a function of dosed (A) Mg-free and (B) Mg-bearing calcian solutions (see text).

In addition to affecting the point of nucleation relative to supersaturation state, the presence of smectite influenced the phase of the precipitate: in the Mg-free solution we observed the immediate formation of calcite in the presence of smectite, whereas vaterite was the first precipitating phase from the homogeneous solution. From Mg-bearing solutions aragonite precipitated both in the presence and absence of smectite.

The aragonite precipitates that formed from Mg-bearing solutions (that were representative of Lake Balaton water) were aged in their mother solutions for 6 months. No change was observed in the smectite-free solution. However, in the presence of smectite peculiar composite particles formed that consisted of three phases: (1) fibrous bundles consisting of protodolomite nanoplatelets, with (2) a single crystal low-Mg-calcite core, and (3) smectite nanoflakes both among the fibers and incorporated into the core calcite (Fig. 4).

We interpreted these observations on the basis of information from the MD simulations described in 1.2 above: ionic clusters were efficiently anchored on the charged surface of smectite, thereby enhancing calcite nucleation. During aging the original aragonite particles partially dissolved and reprecipitated, forming the protodolomite fibers. Additional dissolution/reprecipitation cycles resulted in the dissolution of metastable protodolomite, and a calcite core formed, again assisted by the smectite flakes. We consider the results of these laboratory experiments the most significant part of our work, since they reproduced (partially) ordered dolomite (protodolomite) under ambient conditions.

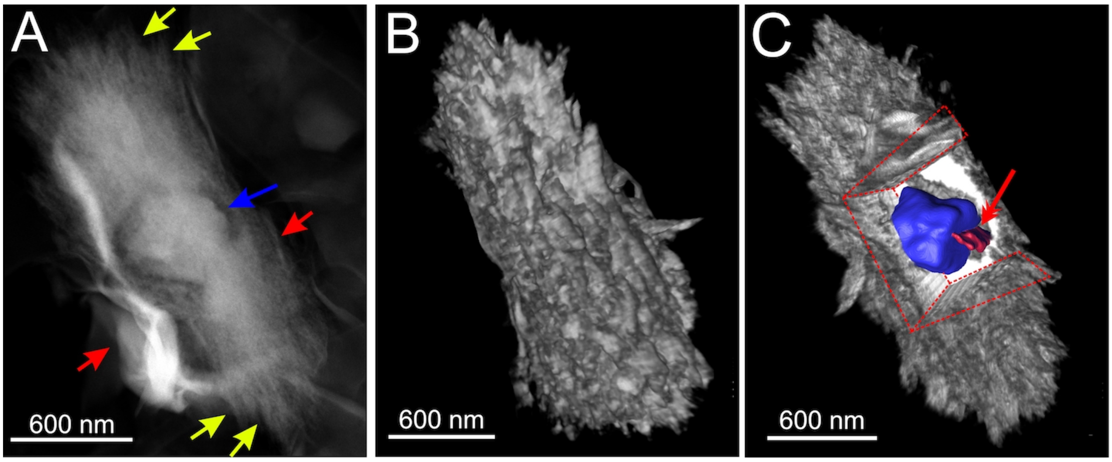

Fig. 4. Composite particle of bundle-like Mg-Ca-carbonate (protodolomite) fibers surrounding a single crystal low-Mg-calcite core, formed after aging the precipitates for 175 days. (A) STEM HAADF image; blue, yellow and red arrows mark the core, fibers and smectite flakes, respectively; (B) and (C) Electron tomographic 3D reconstructions of the bundle-like protodolomite aggregates and calcite cores with interwoven smectite flakes (red arrow); in (C), a window was cut in the external fibers as shown by the red wire frame, in order to expose the core calcite (in blue) with associated smectite (in red).

The results of laboratory carbonate precipitation experiments will be published in a paper that was accepted in EPSL:

Molnár, Zs., Pekker, P., Dódony, I., Pósfai, M. (2021) Clay minerals affect calcium (magnesium) carbonate precipitation and aging. **Earth and Planetary Science Letters**, in press.

2. Dolomite formation in Lake Balaton

Before starting this project, we already noted the presence of anomalous dolomite in the Eastern (Siófok) Basin of the lake on the basis of cell parameters obtained from X-ray diffractograms (Tompa et al. 2014). The occurrence of this dolomite in the most Mg-rich part of the lake suggested that it precipitated from the lake. The aim of the current project was to characterize this phase in more detail. However, this task was difficult, since anomalous dolomite is a minor phase within the Mg-calcite dominated sediment. Therefore, we employed various strategies, including selective dissolution of carbonate phases, the direct TEM study of material collected from the lake, and the laboratory work discussed above under 1.3 as well.

2.1 Selective dissolution procedures aiming to enrich dolomite from sediment samples

Dissolution of the more soluble calcite vs. less soluble dolomite by using weak acids is a well-known procedure used in isotope geochemistry. Typically, acetic acid, HCl, EDTA or phosphoric acid are used. However, we noticed that none of the standard procedures work in our case, when the goal is to enrich minor, submicrometer anomalous dolomite in a matrix of larger calcite grains. Therefore, we wished to systematically explore how grain size affects the dissolution procedure. Acetic acid, HCl and EDTA were tested on mixtures of calcite and dolomite of various size ranges. Indeed, we found that none of these techniques could separate the submicrometer anomalous dolomite from the rest of the sediment (Fig. 5). Still, 1M HCl worked the best.

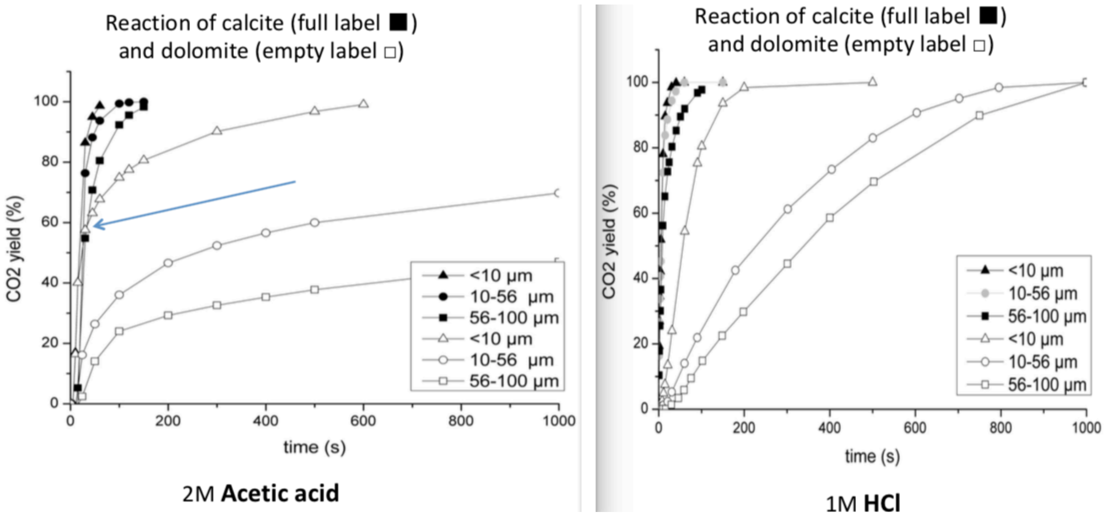

Fig. 5. Dissolution over time of calcite and dolomite grains of various size ranges in 2M acetic acid and 1M HCl. As seen from the curve for <10 um dolomite, its separation from calcite is impossible without losing most of the material of interest.

The dissolution experiments were performed as a student project, and the results are available as an MSc thesis:

Rácz, K. (2019) Kalcit és dolomit oldhatóságának szemcseméret-függése. **MSc szakdolgozat**, Pannon Egyetem, Veszprém.

2.2 Anomalous dolomite ('protodolomite') from Lake Balaton

Since enrichment procedures were not really successful, we tried to identify individual patricles of anomalous dolomite in the samples obtained from suspended matter from the Eastern Basin. Indeed, even though this phase constitutes a minor fraction of the total suspended matter, by using STEM-EDS element mapping for finding Mg-rich carbonate particles we were able to identify and characterize submicrometer dolomite-like particles. In agreement with earlier XRD patterns that showed dolomite-type "order reflections" (such as 1-10 and 015; Gregg et al., 2015), electron diffraction also indicated the presence of *b*-type reflections that do not occur in calcite (Fig. 6). Thus, at least partially ordered Mg/Ca arrangements do occur in this material.

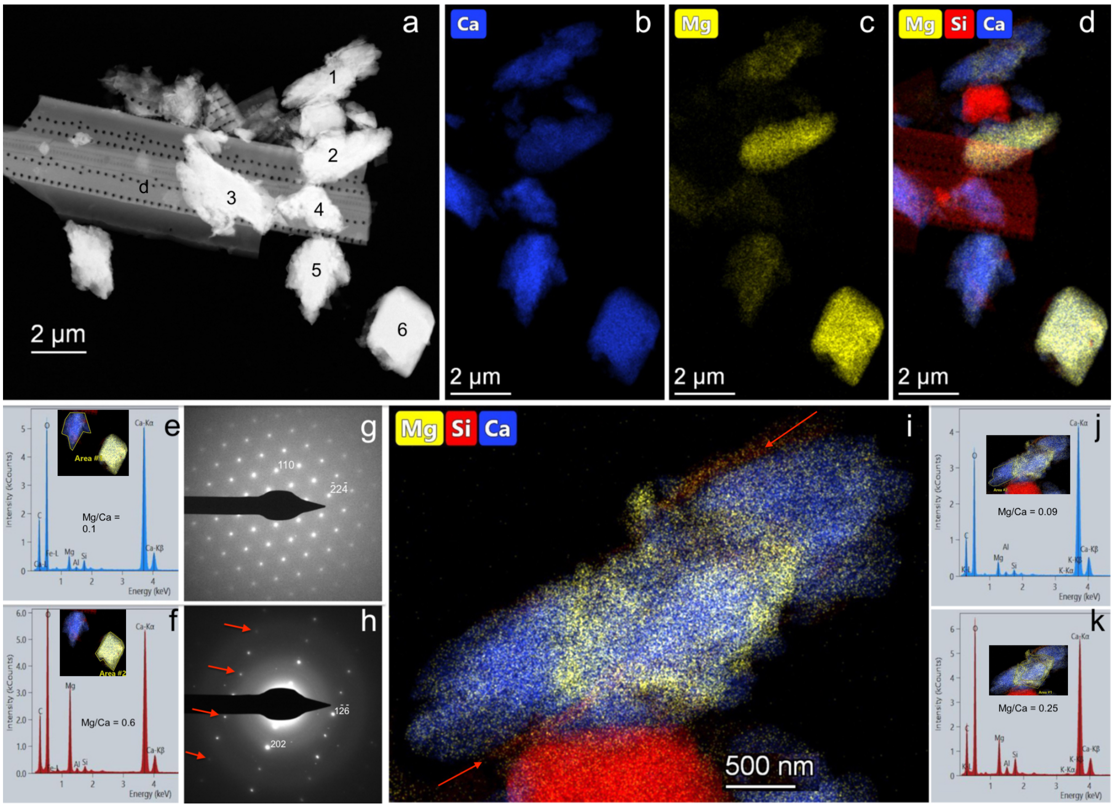

Fig. 6. TEM analysis of protodolomite and low-Mg-calcite particles in suspended matter. Particles marked 2 and 6 (a) have compositions consistent with high-Mg-calcite (b, c, d, f) but their SAED patterns show dolomite-type ordering reflections (h), whereas particles # 1, 3, 4, 5 are low-Mg-calcite. Low-Mg-calcite particles with zones of high Mg content also occur (particle #1 shown in i, j, k).

Nevertheless, the compositions of these particles are typically significantly Ca-rich compared to that of stoichiometric dolomite. In particle F shown in Figure 6, the Mg/Ca ratio is only 0.6, yet the SAED pattern shows ordering reflections (marked by arrows in panel h). Because of the anomalous (Ca-rich) composition relative to dolomite but the presence of ordering reflections, we use the term “ protodolomite” for this phase (in agreement with the original definition by Gaines, 1977).

The structures of protodolomite particles were further studied using high-resolution STEM HAADF imaging. These studies were done on samples (1) from a drillcore that was taken (by a team led by Enikő Magyari) in January 2017 when Lake Balaton was covered by ice, and (2) Lake Fertő sediment samples, provided by Patrick Meister (U. Vienna). The reason why we performed studies on these two types of samples is that the relative amount of protodolomite was much larger in certain Mg-rich layers of the drillcore and in the entire Fertő sediment than in the suspended matter collected from Lake Balaton over the last few years. The results of the structural analysis of protodolomite will be reported below in section (6). We note that even though protodolomite is a very minor component of today’s carbonate precipitation in Lake Balaton, its particles observed in current suspended matter were no different from the ones in the Fertő and drillcore samples; therefore, the main conclusions of the structural studies hold for the currently precipitating protodolomite as well: Mg-Ca ordering occurs in nm-scale domains that have no distinct boundaries.

Concerning the evidence for the current formation of protodolomite, the following arguments can be listed:

- protodolomite is present in current suspended matter in the Eastern Basin

  where the dissolved Mg/Ca ratio is larger;
- protodolomite is distinct from Triassic dolomite in terms of grain size (much smaller), composition (Ca-rich), and structure (ordering in domains);
- protodolomite also occurs within grains of low-Mg-calcite, either as rims around Mg-calcite, or as cores inside Mg-calcite, or as distinct zones within it (see Fig. 6i; we attribute these rhytmic changes in Mg content and structure to dissolution/reprecipitation cycles (Ruiz-Agudo et al., 2014);
- protodolomite was also observed in our laboratory aging experiments (see section 1.3) that intended to simulate conditions in Lake Balaton.

We believe our work on protodolomite is significant, since it documents the curent formation of a dolomite-like phase (that was atributed in the past to sediment processes – Müller (1970)). We aim to publish a paper in a high-impact journal. However, as seen from the above, the identification and characterization of protodolomite, as well as the efforts to obtain an understanding of its formation are related to three types of samples, each originating from the works of different groups. Therefore, the coordination of this planned paper has just started and we aim for submission by the end of the summer of 2021. So far we have published fragments of this topic in the papers mentioned in section (3), and in the conference abstracts listed below:

Pósfai, M., Molnár, Zs., Pekker, P., Rácz, K., Dódony, I., Pálfi, I., Kristály, F., Meister, P., Frisia, S., Magyari, E. (2021) Protodolomite: structure and formation in lakes. **Goldschmidt2021**.

Pósfai, M., Pekker, P., Molnár, Zs., Dódony, I., Frisia, S., Meister, P. (2020) Intraparticle heterogeneity of composition and structure in Ca–Mg carbonate minerals precipitating from a shallow, alkaline lake. **European Microscopy Congress, Copenhagen**, 956. DOI 10.22443/rms.emc2020.956.

Pósfai, M., Molnár, Zs., Pekker, P., Dódony, I.,. Frisia, S., Meister, P. (2019) Microstructure of magnesium-bearing carbonates precipitating from shallow freshwater lakes. **Geological Society of America Annual Meeting, Phoenix**, AZ, 21-25 September. Geological Society of America Abstracts with Programs. Vol. 51, No. 5, ISSN 0016-7592, doi: 10.1130/abs/2019AM-335892.

3. Significance of carbonate mineral precipitation and deposition in Lake Balaton

We wished to understand the current magnitude of carbonate formation in the lake (this part of the research was primarily done by Ágnes Rostási, supported by her OTKA PD grant that had several links to the current project). Therefore, we systematically studied suspended matter and water chemistry at the mouths of tributaries and in the lake for over two years. In addition, rainwater was collected and its solid content measured, and data for dry deposition also assembled. In this way, we obtained a dataset for estimating the mass of annually deposited material from various sources: allochtonous particles from tributaries and the atmosphere contribute about the same mass of material to the sediment annually (estimated between 25 and 40 thousand tonnes each), while carbonates precipitating within the lake contribute vastly more material. When the total amount of precipitating carbonate is calculated by extrapolating the mass measured in the sporadically obtained suspended matter samples, and extrapolating these values over the entire year, 430 thousand tonnes of calcite, corresponding to 2.7 mm/year pure carbonate sediment results. However, if the estimation is based on the measured water chemistry in tributaries, lake, and the

Sió canal, and the amount of precipitating carbonate is based on the total Ca and Mg annually remaining in the lake, a much larger number results: 1.5 million tonnes of dolomite, corresponding to 0.88 mm/year consolidated sediment thickness. This number is significantly higher than suggested by the thickness of holocene sediments in Lake Balaton (Cserny et al., 1991), raising the issue of whether we severely overestimated the amount of precipitating carbonate, or current carbonate formation is much more intense than over most of the history of the lake.

We know that carbonate precipitation is an indirect consequence of photosynthesis by algae (Thompson et al., 1997). As described above in (1) and (2), low-Mg-calcite is the major carbonate mineral that precipitates from the lake, with minor protodolomite also forming in places with high Mg/Ca contents. Both are associated with nm-scale flakes of smectite (present in the water because of its shallowness), indicating the significant role of heterogeneous nucleation. The resulting narrow grain size distribution affects the feeding of filtering organisms, limiting their abundance in the lake. Lake Balaton thus showcases an intriguing interplay of biogenic and inorganic factors in sediment formation and sediment-organism interactions.

These interactions were emphasized in a book chapter in a volume commemorating Lajos Lóczy. In addition, we published a review paper summarizing our results on Lake Balaton sedimentation, in a special volume celebrating the 150-year history of Földtani Közlöny. The results about our "mineral budget" calculations were included in a manuscript that was revised several times and will be submitted in April 2021:

Pósfai M., G.-Tóth L. (2020) A Balaton iszapjának ásványai. In: **A Balaton kutatása - Lóczy Lajos nyomdokán**, Babinszki, E. és Horváth, F. szerk., Magyarhoni Földtani Társulat, Budapest, 233-250.

Pósfai M. (2020) A Balaton üledékének ásványai. **Földtani Közlöny**, 150/4, 511-528.

Rostási, Á., Fodor, M., Rácz, K., Topa, B., Molnár, Zs., Weiszburg, T., Pósfai, M. (2020) Pathways of carbonate sediment accumulation in a large, shallow lake. To be submitted to **Journal of Sedimentary Petrology**.

4. Carbonate biominerals – mussels and otoliths – from Lake Balaton

By following the planned lines of study during the project, new problems arose, some of which were related to carbonate biominerals. In particular, we noted the absence of aragonite in the suspended matter and sediment, despite (1) aragonite formation in our laboratory precipitation experiments, and (2) the presence of an immense amount of invasive mussels (*Dreissena*) in the lake, possessing aragonite shells (Báldi et al., 2019; Balogh et al., 2018). Another question arose from communications with the researchers at the Balaton Limnological Institute – they wished to understand whether fish otoliths can be used as proxies of environmental changes (Campana, 1999).

4.1 Potential dissolution of Dreissena shells

We conducted a student study (MSc thesis research), co-supervised by Dr. Csilla Balogh (Balaton Limnological Institute) on the potential dissolution of *Dreissena* shells. The study has a field and a laboratory component. Empty shells were bagged and placed in the lake for several months, then recovered, their mass measured and dissolution features studied using SEM. The laboratory study included controlled dissolution of shells in carbonic acid and HCl solutions, as well as in lakewater. The main results can be listed as:

- all samples deposited in the lake lost some mass, but the mass loss was highly variable, ranging from a few % to 40% in 4 months;
- laboratory dissolution eperiments revealed typical dissolution features in the nacreous layer, and confirmed that even in lakewater some dissolution occurs;
- dissolution grooves in the lake-deposited shells showed identical features to those of the lab-dissolved shells (Fig. 7).

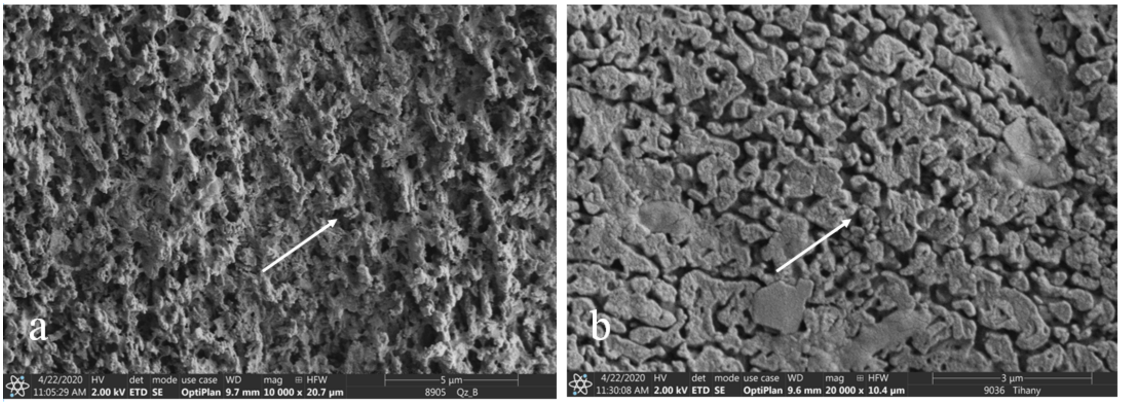

Fig. 7. SEM images of the nacreous (inner) surface of shells (a) after dissolution by HCl(aq) and (b) dissolution by lakewater. The arrows point to etch pits produced during the dissolution.

In summary, according to our rough estimate the half-life of spent shells in Lake Balaton is about 4 years, explaining why no significant aragonite accumulation can be observed in the sediment.

Another interesting observation we made by performing TEM studies on *Dreissena* shells is their densely twinned microstructure, and the presence of polytypic sequences in aragonite. These features formed the basis of a new research proposal that was submitted with a Slovenian collaborator.

The results on the dissolution and nanostructure of *Dreissena* shells were so far included in an MSc thesis and conference abstracts, but we plan to write a paper on the dissolution, and explore the nanostructure further:

Nyokabi, W. (2020) Potential dissolution of calcim carbonate shells in a freshwater environment. **MSc Thesis**, University of Pannonia, Veszprém.

Molnár, Zs., Pekker, P., Jakab, M., Dódony, I., Vitál, Z., Pósfai, M. (2020) Nanostructure of biogenic aragonite: a study of otoliths and bivalve shells from a freshwater environment. **European Geosciences Union Annual Meeting, Vienna**.

4.2 Growth features and microstructures in fish otoliths

Otoliths are $CaCO_3$ grains within the inner ears of bony fish. Since otoliths grow continously over the lifetime of fish, their compositions are supposed to reflect environmental conditions that the fish experienced (Kern et al., 2017). We studied otoliths from two specimens, a dwarf catfish and a pike-perch from Lake Balaton. The former was used as a reference material, since the age of the fish was known (3 years). By studying the „growth rings" using optical microscopy and SEM, we tried to identify annual, seasonal and even shorter time periods in the hierarchical bands of different contrast. However, an accurate identification of time periods is difficult, since some bands terminate, some diverge into two bands, and in general are much less regular than tree rings, for example. No compositional variations were observed. However, very interesting nanostructural features were fond in the aragonite: domains with slightly different crystallographic orientation were separated by bands of voids, and non-aragonitic extra reflections were observed in electron diffraction patterns. These structural features are planned to be studied further, while the observations on the growth features have been included in a student competition (TDK) and will be used in a BSc thesis (to be submitted in May 2021):

Kövér, R. (2020) Otolit növekedési zónáinak vizsgálata: szerkezeti sajátosságaik és környezetjelző szerepük. **TDK dolgozat**, University of Pannonia.

Molnár, Zs., Pekker, P., Jakab, M., Dódony, I., Vitál, Z., Pósfai, M. (2020) Nanostructure of biogenic aragonite: a study of otoliths and bivalve shells from a freshwater environment. **European Geosciences Union Annual Meeting, Vienna**.

5. Characterization of Mg-rich carbonates in a lake sediment core

In the winter of 2017 three undisturbed sediment cores were retrieved from the Szemes Basin of Lake Balaton, by a group led by Dr. Enikő Magyari (ELTE), with the aim of studying the core using novel research techniques for a modern reconstruction of paleoclimatic and environmental conditions during the history of the lake. The sediment sequence covers the Holocene and Late Glacial period, and it extends back to ~16,000 cal yr BP. X-ray fluorescence spectrometry (XRF) was used to reconstruct rapid changes in the element content of the lake sediment. Our group contributes to this research by performing transmission electron microscopy (TEM) studies on specimens from the layers of Mg enrichments occurring around 5500 kal BP and 8100 kal BP years. TEM data show good agreement with the results of both XRF and XRD measurements, with an increased proportion of protodolomite around 5500 cal BP 8100 cal BP, likely indicating drier climatic conditions (Fig. 8). These results were also verified by oxygen isotope studies.

In addition to the original goal of a climate reconstruction, we also plan to use the sediment core material from the two Mg-rich layers for our planned comprehensive study on protodolomite nanostructure (and formation). The material is also perfect for a comparison of XRD and TEM techniques in the study of the compositions of Mg-bearing carbonates (Fig. 8).

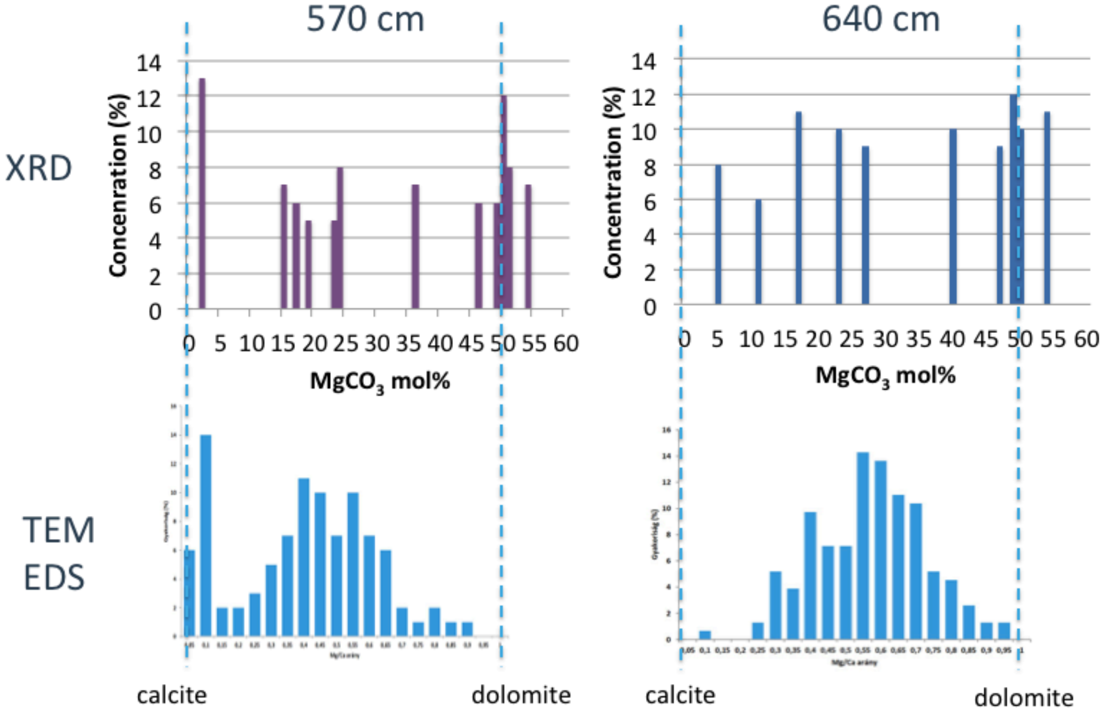

Fig. 8. Compositional analysis of Mg-bearing carbonates from two Mg-rich sediment layers at 570 and 640 cm depth (5500 and 8100 cal BP years, respectively). The upper panels show the distribution of relative concentrations of several phases with various Mg contents, used for modeling the profile of a broad peak in the XRD diagram between calcite and dolomite d(-104). The lower panels illustrate the Mg contents of individual particles as measured using STEM-EDS. Differences between the two samples and between the XRD and TEM results are evident, and are the subject of future analysis.

So far a conference abstract resulted from this joint work but several significant publications are anticipated in 2021 and 2022:

Pálfi, I., Pósfai, M., Kristály, F., Veres, D., Arnaud, F., Szalai, Z., Gresina, F., Szabó, Z, Darabos, G., Korponai, J., Czuppon, Gy., Demény, A., Magyari, E. (2021) Geochemical survey of Lake Balaton sediments: Holocene paleoenvironment and paleoclimate. **EGU General Assembly**, online, 19-30 April, EGU21-15654.

6. Structural studies on protodolomite from Lake Fertő

During the run of this project an opportunity arose to obtain more information on freshwater dolomite formation: Dr. Patrick Meister from University of Vienna (and Dr. Silvia Frisia from U. Newcastle, Australia) approached us to perform TEM analysis on Lake Fertő sediments. Lake Fertő is a similar but chemistry-wise more concentrated system than Lake Balaton where a full range of Mg-bearing carbonates occur from low-Mg calcite to dolomite, and high-Mg calcite and anomalous dolomite are major components of the sediments (Fussmann et al., 2020). We performed TEM analyses of Lake Fertő carbonates with the goal of obtaining microstructural and compositional details over the last two years.

Elemental maps show a wide range of Mg/Ca ratios, both between and inside individual particles: an analysis of 400 particles produced an essentially continuous distribution from almost stoichiometric calcite to a slightly Ca-rich dolomite composition. A striking feature of some particles is intraparticle compositional heterogeneity: distinct changes in the Mg/Ca ratio can be observed, typically (but not exclusively) in concentric zones (Fig. 9). In such particles the Mg-rich zones have dolomite-like compositions (Mg/Ca atomic ratio close to 1), whereas the rest of the particle displays a variety of Mg/Ca atomic ratios up to about 0.5. These compositional variations are reflected in structural changes as well: whereas SAED patterns obtained from the less Mg-rich regions show no ordering reflections, patterns from the Mg-rich regions typically display order reflections (such as the 003) typical of the dolomite structure.

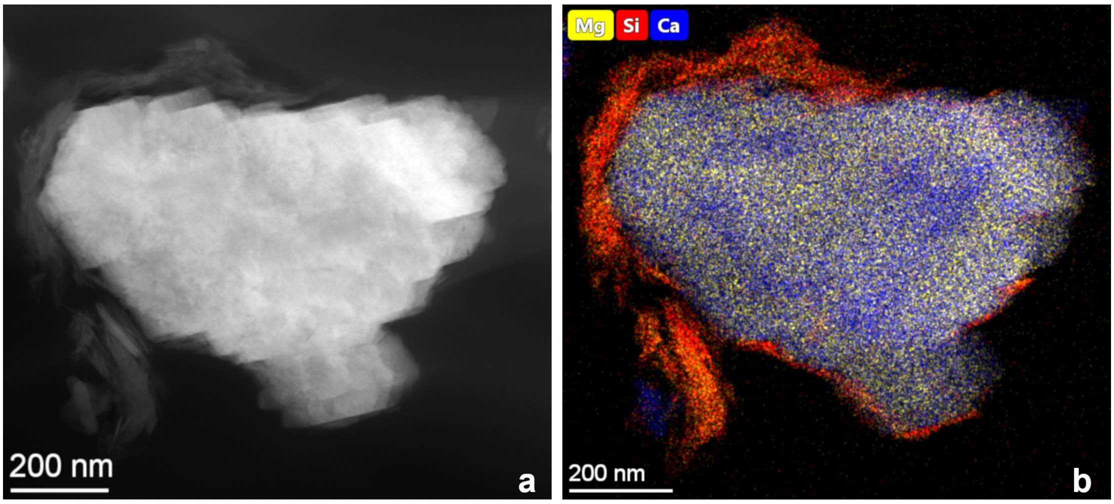

Fig. 9. (a) HAADF image and (b) STEM-EDS elemental map of a typical carbonate particle from the sediment of Lake Fertő. As indicated by the distribution of Si, the particle is rimmed by a thin veil of the clay mineral smectite. Intraparticle compositional heterogeneity is visible by the variation of predominantly yellow and blue zones that correspond to Mg-bearing calcitic and dolomitic compositions, respectively.

High-resolution TEM and HAADF images reveal an additional structural complexity within the Mg-rich zones, suggesting that the degree of Mg/Ca ordering varies on the nm scale. Figure 10a shows a high-resolution HAADF image (obtained with the electron beam parallel to the calcite [100] direction), in which individual cation columns are resolved as dots with bright contrast. Since the intensity of each dot is directly related to the square of the total atomic number (Z^2) within the column, an ordered alternation of Ca and Mg columns will produce dots with strong and faint contrast, respectively, whereas a disordered arrangement of Ca and Mg will produce dots with equal contrast. As seen from the example shown in Figure 10b, nm-scale domains (less than 5 nm in diameter) with ordered arrangements of Ca and Mg ions alternate with disordered (or less ordered) domains of similar sizes. Thus, our results suggest that nm-scale ordered protodolomite forms in the lake.

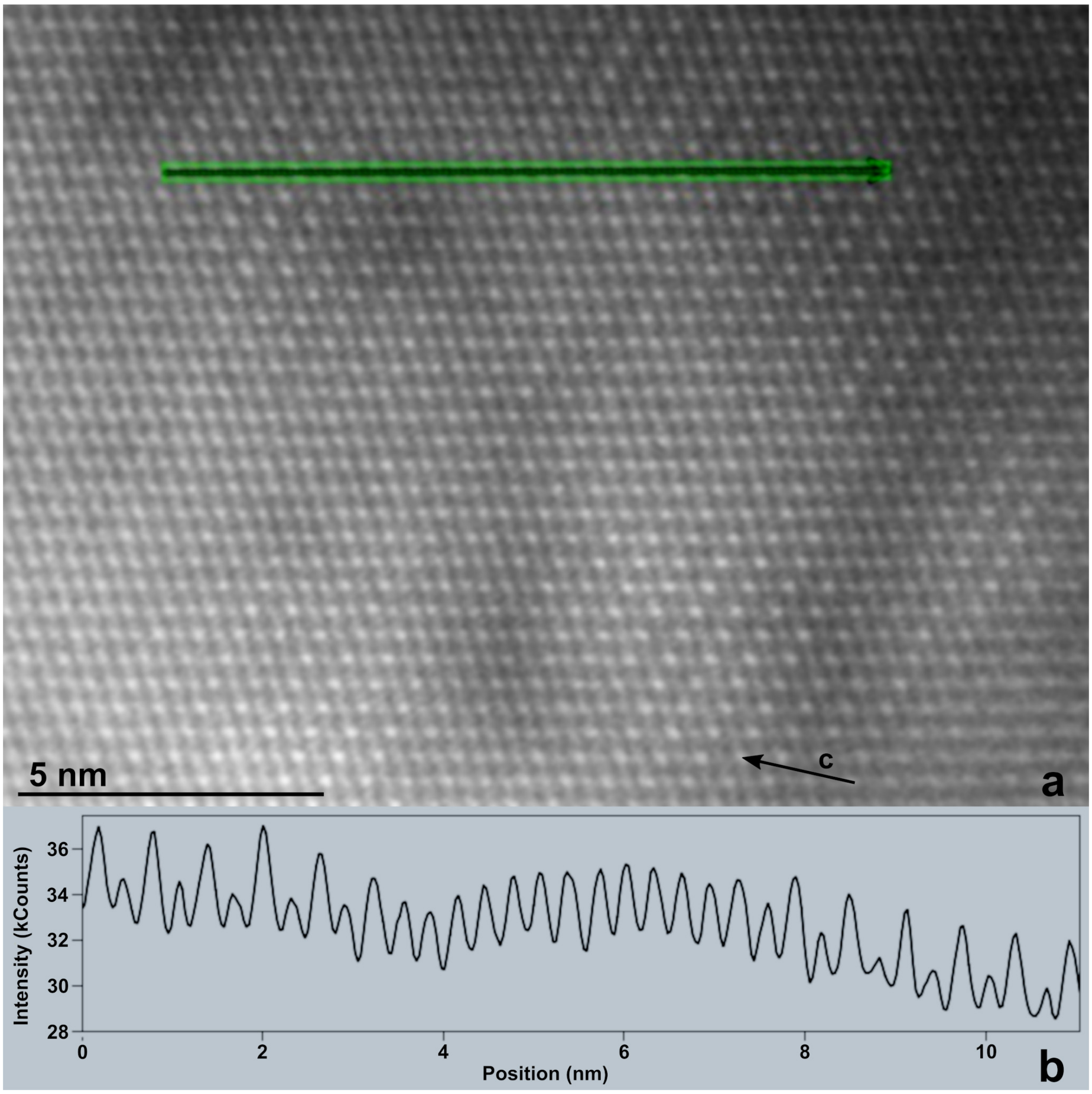

Figure 10. (a) High-resolution HAADF image obtained from a region of a carbonate particle with dolomitic composition, indicating nm-scale domains of ordered and disordered arrangements of Ca and Mg. (b) Intensity profile of image contrast along the line shown in (a), suggesting the presence of alternating Ca and Mg atomic columns on the two sides, and no ordering (atomic columns with approximately equal numbers of Ca and Mg atoms) in the middle of the section.

A huge amount of work was done on the Lake Fertő sediment and – in our opinion – very interesting results obtained; nevertheless, the backgrounds of the collaborating partners are relatively distant (Dr. Meister's in sedimentology and ours in mineralogy/crystallography), resulting in difficulties to form a consensus opinion about data interpretation; even after several versions of a ms were prepared, the results have been published in conference proceedings only. Independent of the fate of the paper being prepared on Lake Fertő carbonates, we plan to use some of our TEM results on material from Lake Fertő together with the data on protodolomite from Lake Balaton (precipitated both currently and in the past) to compose a paper specifically on protodolomite structures.

Pósfai, M., Molnár, Zs., Pekker, P., Rácz, K., Dódony, I., Pálfi, I., Kristály, F., Meister, P., Frisia, S., Magyari, E. (2021) Protodolomite: structure and formation in lakes. **Goldschmidt2021**.

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Pósfai, M., Molnár, Zs., Pekker, P., Dódony, I.,. Frisia, S., Meister, P. (2019) Microstructure of magnesium-bearing carbonates precipitating from shallow freshwater lakes. **Geological Society of America Annual Meeting, Phoenix**, AZ, 21-25 September. Geological Society of America Abstracts with Programs. Vol. 51, No. 5, ISSN 0016-7592, doi: 10.1130/abs/2019AM-335892.

Meister, P., Pósfai, M., Pekker, P., Molnár, Zs., Neuhuber S., Demény, A., Gier, S., Frisia, S. (2019) Mineralogy and nano-structure of modern dolomite in Lake Neusiedl. **European Geosciences Union General Assembly, Wien**, 7-12 April. Geophysical Research Abstracts 21, EGU2019-13171.

Benefits of the research program beyond the actual science results

The topic of the present research project was relatively new for us, and the complexity of the science problems related to carbonate minerals and Lake Balaton, in particular, became only apparent during the course of the study. Therefore, the research branched out into several new directions, and the scope of our efforts became wider than originally planned. Consequently, some of the most important results have yet to be published. But even beyond the actual research output (which we consider reasonably good), the project was highly important for our Environmental Mineralogy Research Group in a number of ways. These are listed below.

Student involvement

The project was highly useful for providing science topics for students. Carbonate precipitation in Lake Balaton or related themes were studied in the following student projects:

Student competition (TDK) study:

- Molnár Zsombor: A heterogén kristálynukleáció vizsgálata a balatoni kalcit példáján – képződés, morfológia, összetétel. 2017-18 (institutional and national (both OFKD and OTDK) 1st prizes; supervisors: Mihály Pósfai, Tamás Váczi)
- Kövér Regina: Otolit növekedési zónáinak vizsgálata: szerkezeti sajátosságaik és környezetjelző szerepük. 2020 (institutional 1st prize; supervisors: Zsombor Molnár, Mihály Pósfai).

BSc Thesis research:

- Berkes Martina: Mg-kalcit és dolomit közötti fázishatár kijelölése termodinamikai modellezéssel. BSc Thesis, University of Pannonia, Institute for Material Engineering, 2016 (supervisor: Ilona Nyirő-Kósa).
- Kövér Regina: Otolit növekedési zónáinak vizsgálata: szerkezeti sajátosságaik és környezetjelző szerepük. BSc Thesis, University of Pannonia, Research Institute for Bio-nanotechnological and Chemical Engineering (supervisors: Zsombor Molnár, Mihály Pósfai) – to be completed in May 2021.

MSc Thesis research:

- Molnár Zsombor: A balatoni kalcitképződés laboratóriumi vizsgálata. MSc Thesis, ELTE TTK, Dept. of Mineralogy, 2018 (supervisors: Mihály Pósfai, Tamás Váczi).
- Rácz Kornél: Kalcit és dolomit oldhatóságának szemcseméret-függése. MSc Thesis, University of Pannonia, Dept. of Earth and Env. Sciences, 2020 (supervisor: Mihály Pósfai).
- Winfred Nyokabi: Potential dissolution of calcium carbonate shells in a freshwater

environment. MSc Thesis, University of Pannonia, Dept. of Earth and Env. Sciences, 2020 (supervisors: Mihály Pósfai and Csilla Balogh).

PhD research:

- Melinda Fodor: Molecular dynamics simulations of calcium carbonate nucleation on clays. (predoctoral research theme that helped her to complete earlier PhD work on another topic; supervisor: Mihály Pósfai)
- Zsombor Molnár: Heterogeneous nucleation of calcium carbonate polymorphs. University of Pannonia, started in 2018 (in progress; supervisor: Mihály Pósfai).
- Kornél Rácz: Phosphorus contents of lake sediments. University of Pannonia, started in 2020 (in progress; supervisor: Mihály Pósfai).
- Ivett Pálfi: Geochemical characterization of the sediments of Lake Balaton: Holocene paleoenvironment and paleoclimate. ELTE, started in 2019 (in progress; supervisor: Enikő Magyari, consultant: Mihály Pósfai).

Research infrastructure

During the course of the project a brand new electron microscopy laboratory was established at UP (the “Nanolab”) under the leadership of the PI (funded by a GINOP infrastructure project). This is a major progress in research infrastructure, and the OTKA project was useful for providing immediate science problems for the new lab and, on the other hand, the project benefited greatly from the new facilities. Some of the problems in this research presented special challenges (such as the electron beam-sensitive nature of carbonates), and several special techniques (including high-resolution STEM HAADF imaging and simulation of such images, plus STEM electron tomography for 3D morphological reconstruction) were first tried and tested on materials (and problems) related to this project. In this way, the OTKA project greatly helped us to build the necessary experience and to obtain the know-how needed to run our new Nanolab.

In addition, an automatic titrator was installed in 2019 (from another GINOP project) that was extensively used in the current research, for the tasks detailed under 1.3 above.

Introduction of new research techniques

Assisted by this research project, we ventured into new fields that were formerly not represented in the research repertoire of our group:

- Molecular dynamics simulations: with the help of our chemist colleagues at UP (Tamás Kristóf and Zoltán Ható) we could perform theoretical calculations on cluster formation in calcian carbonate solutions and simulate their formation and behavior in the presence of heterogeneous surfaces. This technique will be used in the future in other environmental mineralogy problems as well.

- Experimental lab precipitation using an automatic titrator: this technique was introduced to nucleate carbonates under controlled conditions, and PhD student Zsombor Molnár trained himself to become and expert. He is currently using the titrator on a daily basis for testing various experimental setups in systems simulating the water and sediment of Lake Balaton. Currently these experiments are designed to study the fate of phosphate in such systems, its physical and chemical effects on carbonate precipitation, and the conditions that lead to the binding and release of phosphorus from sediment minerals.

- New TEM techniques: as mentioned above, carbonate minerals and their complex associations provided excellent materials for developing and testing optimal operation parameters for high-resolution HAADF imaging and STEM-HAADF electron tomography. The expert in these techniques is Péter Pekker, and his experience will be used in new research lines on aragonite and cave carbonates, topics that developed from the current project (see below).

New collaborations

In the course of the project several new collaborations were initiated. We list these below according to the specific subprojects, in the same order as presented in the Results section.

1.1 HR SEM measurements were done in Ljubljana, at the Jozef Stefan Institute by Maja Koblar, whereas HR STEM work by András Kovács in Jülich (at that time we still did not have our own electron microscopy lab).

1.2 As mentioned above, a new research technique, molecular dynamics simulations were performed with the help of Tamás Kristóf and Zoltán Ható (UP); based on the success of this joint work, a new collaboration was initiated with them on the structure of kaolinite nanoscrolls (published in Applied Clay Science).

1.3 For interpreting the LaMer curves that resulted from the titration experiments, Zsombor Molnár initiated consultations with Denis Gebauer (U. Hannover), a well-known expert in experimental acqueous mineral chemistry. Dr. Gebauer presented a talk in our 2021 Winter School in Mineral Sciences as well, and we hope to remain in touch with him in the future.

2. Our planned study on protodolomite involves the collaborating groups mentioned below under #5 and #6.

3. XRD studies were performed at the Dept. of Mineralogy, ELTE, by Boglárka Topa and Tamás Weiszburg. In addition, a book chapter resulted from this work, with László G.-Tóth (Balaton Limnological Institute, Tihany) as coauthor.

4. Projects on carbonate biominerals were started together with researchers from the Balaton Limnological Institute, Tihany; the MSc thesis work on mussels was co-supervised by Csilla Balogh, while Zoltán Vitál’s contribution is essential to the research on fish otoliths.

5. A new collaboration was started with Enikő Magyari and Ivett Pálfi (ElTE) on the sediment core taken from Lake Balaton in 2017. Ivett Pálfi is co-supervised by the PI of this project.

6. The study of carbonate minerals from Lake Fertő was intitiated by Patrick Meister (U. Vienna) who also brought Silvia Frisia (U. Newcastle, Australia) into the project. In addition to the work discussed above, we extensively studied Silvia Frisia’s various carbonate specimens: dolomite from Italy, aragonite from modern stromatolites, and calcite/silica composites from Antarctica. Work on these research topics is currently in progress and we hope to include these themes in new research proposals.

New research proposals

1. OTKA grant for studying phosphorus cycling (started January 2021, PI: Vera Istvánovics).

Based on our published work on Lake Balaton carbonates, we were invited to join the research effort by a group led by Dr. Vera Istvánovics (Technical University Budapest). The goal is to identify the cause of an unexpected, large algal bloom that occurred in the lake in August-September 2019 (Istvánovics et al., 2021). Our task is to study phosphorus adsorption on and release from carbonate and iron oxide minerals, the prime candidates in the sediment for important roles in phosphorus cycling (Istvánovics et al., 1989). Two PhD students are involved (Zs. Molnár and K. Rácz). We already have very promising initial results on the forms of phosphorous enrichment in Lake Balaton samples and on the role of phosphorus in carbonate precipitation (from lab experiments).

2. Hungarian-Austrian joint OTKA grant on cave carbonates (started January 2021, PI: Péter Németh)

Péter Németh is a regular user of our TEM facilities and invited us into this project that aims to clarify phase transformations in carbonate speleothems, with a focus on their potential uses as paleoclimate indicators.

3. Hungarian-Slovenian joint OTKA proposal on the structure of aragonite (submitted, PI: Mihály Pósfai and Aleksander Recnik)

This is a research proposal that was just submitted. We plan to study aragonite structures: twin boundaries and polytypic modifications from a variety of environments. The proposal was initiated by a convergence of interests of the Hungarian and Slovenian groups (plus including Péter Németh who described a new monoclinic aragonite variety recently). Our interest stems from two of the subtopics described above: the laboratory precipitation experiments (1.3) and the work on carbonate biominerals (4), both of which concern aragonite.

4. Multidisciplinary National Laboratory on Climate Change Research (consortial project, PI at Univ. Pannonia: András Gelencsér)

We became involved in this large-scale effort primarily because of our studies on phosphorus cycling in Lake Balaton, and the relevance of some of our subtopics above to climate change.

In summary, the project helped us greatly in the last 5+ years to perform international-level research. We are grateful to the reviewers and the panels of NKFIH for supporting our original proposal, and the administrative personnel of NKFIH for their prompt and flexible handling of issues that arose during the course of research.

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