Final Report

on National Research, Development and Innovation Office project PD 121088 entitled "Natural and anthropogenic effects on mineral precipitation and deposition in Lake Balaton"

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Scientific background and aims

The formation of carbonate minerals in water is related to the geochemistry of the geological environment, can be mediated by organisms, and may be affected by allochtonous mineral particles originating from natural and anthropogenic sources. The unique features of Lake Balaton provide an example of a freshwater „carbonate factory". **The main question of the research was which factors influence the mineralogical processes in Lake Balaton.** The primary aim of the project was to identify the origins (biogenic or inorganic, allochtonous or autochtonous) of similar carbonate phases. The final goal was to roughly estimate a mineral budget for sedimentation in Lake Balaton (influxes from different sources, sediment formation rates).

To achieve this goal, the following topics were studied during the 3-year research period: **(1)** modeling the nucleation of carbonate species by laboratory experiments; **(2)** determination of the mineralogical influence of the tributaries, **(3)** studying the importance of atmospheric deposition and **(4)** finally assessment of the mineral budget in Lake Balaton.

Results

1. Modeling the nucleation of carbonate species by laboratory experiments

Carbonate mineral formation in lakes is a complex, multivariable process influenced by biogenic and inorganic factors (Obst et al. 2009). **The specific goal of this line of our research was to understand the nucleation of carbonate crystals in Lake Balaton.** By simulating the mineral formation in a controlled environment we investigated the factors (temperature, concentration of ions and other minerals, and the presence of various aquatic organisms) that may influence calcite seeding. In order to achieve the chemical conditions necessary for carbonate production, we used photosynthetic microorganisms. We tested how certain algae and the surfaces provided by other minerals (such as smectite) mediate calcite nucleation, determined the concentrations of chemical species in water by inductively coupled optical emission spectrometry (ICP-OES) and ion chromatography (IC). The precipitation and crystal growth were observed by optical microscope and scanning electron microscope (SEM). The solid phases were characterized using Raman spectroscopy (RS) and transmission electron microscopy with energy-dispersive X-ray spectrometry (TEM EDS). Based on previous results (Perrin et al. 2016) we estimated the Mg content of calcite on the basis of features observed in the Raman spectra.

1.1. Nucleation of carbonates in the presence of aquatic organisms

We studied the roles of microorganisms and pre-existing mineral particles in calcite nucleation. Mineral formation processes in Lake Balaton were reproduced under controlled conditions. It is expected that photosynthesis remove CO_2 and trigger calcite precipitation. Clay minerals provided nutrients for algae and thus resulted in enhanced rates of photosynthesis. The question was that whether clay minerals served as heterogenous nucleation surfaces or they enhanced calcite nucleation. The starting point of our experiments were filtered lakewater, aquatic microorganisms that are available in pure cultures in our institute (*Arthrospira fusiformis*, *Nitzschia palea*, *Scenedesmus* sp.), and montmorillonite. The solutions were stored in covered borosilicate glass containers under natural illumination under

varying conditions (in pure lake-water, with the presence of mud or clay under separated conditions in dialysis tube). We monitored the appearance of precipitates, and if present, newly formed materials were collected for SEM and TEM analyses. Solution chemistry was measured after 1, 4, 7 and 14 days. When the experimental conditions allowed, the samples were examined daily with optical microscope, and by the end of experiments SEM images and EDAX spectra were available. The filtered materials were dried in a desiccator by using silica gel at room temperature.

In the second part of the project we refined the research method in order to determine the role of algae in mineral formation. In the new laboratory experiment particulate material was filtered from lakewater using 0.45 μm mixed cellulose membrane filter. A new diatom culture (*Nitzschia supralitorea Lange Bertalot 1979*) was added to the filtered water. These ones are smaller in size (5 μm) than the previously used algae species. The aim was similar to the former attempt to shift the chemical balance of water towards calcite formation by the photosynthesis of algae. The difficulty of the experimental work stemmed from the fact that the laboratory medium in which the algae were grown was heavily contaminated with minerals of unknown origin (mostly clays) as it also contained soil solution according to the recipe description. The experiment was repeated in one and two week intervals. Temperature and pH of solution were measured every minute with continuous stirring on room temperature, and the change in Ca-ion concentration was recorded by a Ca-selective electrode. All samples were examined with optical microscope and secondary electron SEM images were made of samples that contained calcite particles. The size of formed carbonate minerals are typically about 2–3 μm. The particles characteristically appear to be aggregates of smaller crytallites. The grains consist Mg and Ca based on the EDAX spectra. Although detectable calcite precipitation occurred in one sample, other attempts were unsuccessful due to the sensitivity of algae cultures.

A **summary of the results** reveals that the size of formed carbonate minerals were typically about 2–3 μm. The particles characteristically appear to be aggregates of smaller crytallites. We found that the presence of smectite promotes calcite precipitation, but later the calcite crystals appear also on the surfaces of diatoms. The morphologies and compositions of the calcite crystal vary and depend on the different nucleation sites. We suggest that the nucleation process might be similar as reported in Smeets et al. (2017), which explains the specific properties of the calcite crystals. According to the Raman spectra and TEM EDS results the calcite crystals have high Mg contents (ranging from 5 to 15 mol%), but we cannot identify any dolomite-like Mg ordering. Based on RS, the Mg content of single calcite crystals kept increasing in four months. The results could shed light on the temporal fluctuations of precipitation and the effects of algae on polymorph selection.

1.2. Inorganic experimental calcite crystallization

Although the research plan did not include, to obtain more information about calcite crystallization we also performed experiment in an inorganic way. In vivo biological activities such as photosynthesis and respiration may regulate the dissolved carbon dioxide as well as the rates of nucleation and crystal growth. In vitro, we started experiments with smaller volume of water samples originating from Lake Balaton, and studied the effects of the changes in inorganic composition for the rates of precipitation reactions. On the basis of the systematically measured concentrations of inorganic components in the lakewater, the precipitation reactions between calcium(II), magnesium(II), and carbonate were followed in details.

The temperatures of the samples varied in a wide range (0.9–25.5 °C). The temperature dependency of all equilibrium reactions were taken into account. The total carbonate concentrations were in the range of 130–380 mg l^{-1}. The pH varied between 7.7 and 9.5, therefore the dominant carbonate species was usually the HCO_3^- (16–92 %). The ratio of $CaCO_3$ was lower than 35 % among the carbonate forms (In some cases it was zero). The partial molar percentages of other carbonate forms (CO_3^{2-}, H_2CO_3, CO_2 a.q.) were under 5 % in all samples. The sizes of Ca-Mg carbonate solids were in the colloidal range, and their crystal growth may be hindered, therefore their precipitates did not settle. The total concentration of carbonate / carbon-dioxide was reduced by bubbling argon through the solution overnight, and we measured continuously the temperature and pH. As the consequence of the decrease of solvated carbon dioxide's concentration, the pH started to increase (from the initial 8.1 to 9.8).

In parallel with the evaluation of these experimental data, we made model calculations for wider temperature and pH ranges based on the physical-chemical parameters of the coupled equilibrium reactions. We found that at 25 °C the solution did not contain precipitate (Ca-Mg carbonate solids). The work will be continued with further laboratory experiments (using CO_2 gas for bubbling to reduce pH), and additional model calculations for the better understanding of the carbonate precipitation reactions in the water of Lake Balaton.

2. Mineralogical influence of the tributaries

The geological setting of Lake Balaton is characterized dominantly by carbonate rocks (Budai et al. 1993; Csillag et al. 1995). The mainly dolomitized provenance provides special environmental conditions and partly influences the unique chemical properties of Lake Balaton (e.g. pH=8.5, high dissolved Mg/Ca ratio) by the weathering of the surrounding carbonate-bearing rock formations. We studied the properties and concentrations of allochtonous minerals, in particular the types (compositions, particle sizes and habits) of detrital calcite and dolomite by depositing and filtering particulate material from water samples of selected major inflows. Comparing the geochemical database of the provenance with the particles filtered from water samples reflect the evolution of mineral assemblages from the source area to the sedimentary basin.

2.1. Sampling details

Suspended materials from the main tributaries were collected, complemented with water samples from some streams draining the karstic source area. Although the amount of water delivered by these inflows is small compared to the main inflows (e.g., Zala river, Nyugati-övcsatorna), the chemical composition of water and the features of sediments will give the necessary information to better understand the origin of carbonate minerals in Lake Balaton. We collected samples over a period of two and a half years, from May 2016 to October 2018. In total, 55 samples from Lake Balaton, 11 from the Sió Canal, 107 from tributaries (Fig. 1).

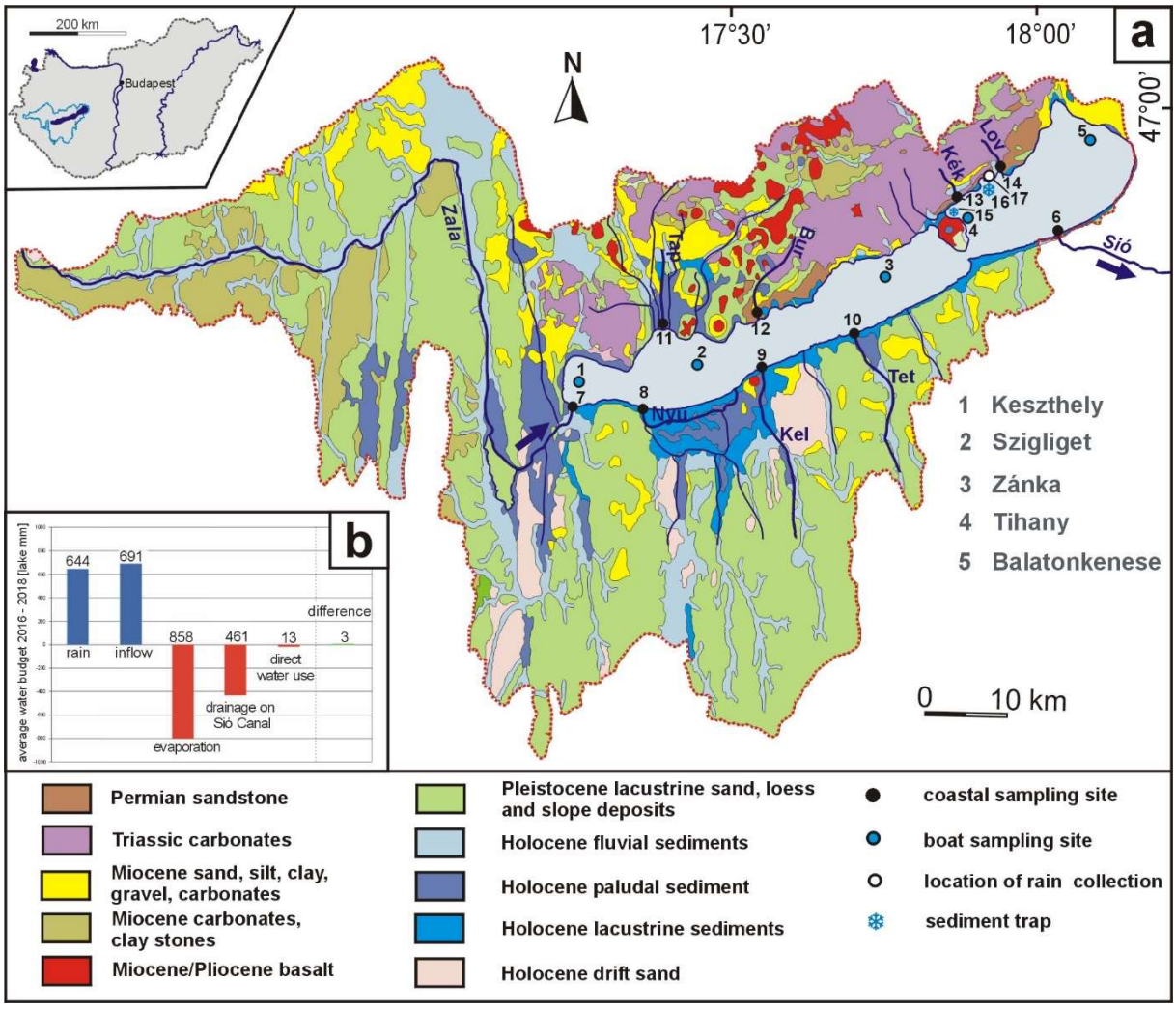

Figure 1 a Simplified geological map of the catchment area of Lake Balaton (after Budai et al. 1999) with sampling sites marked. The location of lake samples is shown by blue dots (1 Keszthely, 2 Szigliget, 3 Zánka, 4 Tihany, 5 Balatonkenese). Black dots indicate coastal water samples derived from the only outflow (6 Sió Canal) and major inflows (7 Zala River, 8 Nyugati-övcsatorna/Nyu, 9 Keleti-bozót árok/Kel, 10 Tetves-patak/Tet, 11 Tapolca-patak/Tap, 12 Burnót-patak/Bur, 13 Kéki Séd/Kék, 14 Lovasi Séd/Los). The two snowflakes show sites (15. Diós Bay, 16. Csopak) where sediment traps were used under ice. White dot marks the location of rainfall collection (17 Csopak). The flow directions of the main tributary (Zala River) and the only artificial outflow (Sió Canal) are also indicated. **b.** Average water budget of Lake Balaton (2016 – 2018).

Four tributaries each on the north and south shores of the lake (Tapolca-patak, Burnót-patak, Kéki Séd, Lovasi Séd and Tetves-patak, Keleti-bozót árok, Nyugati-övcsatorna, Zala River, respectively) were sampled at least 12 times, with the main inflow, the Zala River, sampled more often. From Lake Balaton we collected samples from a boat 15 times, at five locations along the long axis of the lake (Keszthely, Szigliget, Zánka, Tihany, Balatonkenese). During our study period the lake froze over only once, over a four-week period in January and February 2017, providing an opportunity to collect freshly precipitated material, presumably devoid of resuspended sediment. The samples from Sió Canal are of special importance, unique and unrepeatable, because the works for the renovation of the sluice started in 2020. As a result of construction work, extremely large amounts of unknown soil and crushed stone were accumulated in the channel bed directly at the estuary. Large quantities of construction waste making impossible to accurately determine the mineralogical composition of water samples collected later.

Tributaries bring both water and solid particles into the lake. While the chemistry of the former determines mineral-forming processes within the lake, the latter is responsible for delivering a significant fraction of allochtonous constituents of the lake sediment.

2.2. Water chemistry

The measured elemental concentrations of major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}) showed some fluctuations, particularly in the smaller streams. In general, all watercourses were characterized by relatively high concentrations of HCO_3^- (averaging 5.5, 6.2 and 6.4 mmol l^{-1} in the Zala River and in northern and southern shore inflows, respectively), Ca^{2+} (averaging 1.6 mmol l^{-1}) and Mg^{2+} (with averages of 1.4 mmol l^{-1} in the Zala River and 2.1 mmol l^{-1} in the smaller streams). A constrained cluster analysis was carried out on the basis of principal components of main ion concentrations (Fig. 2.).

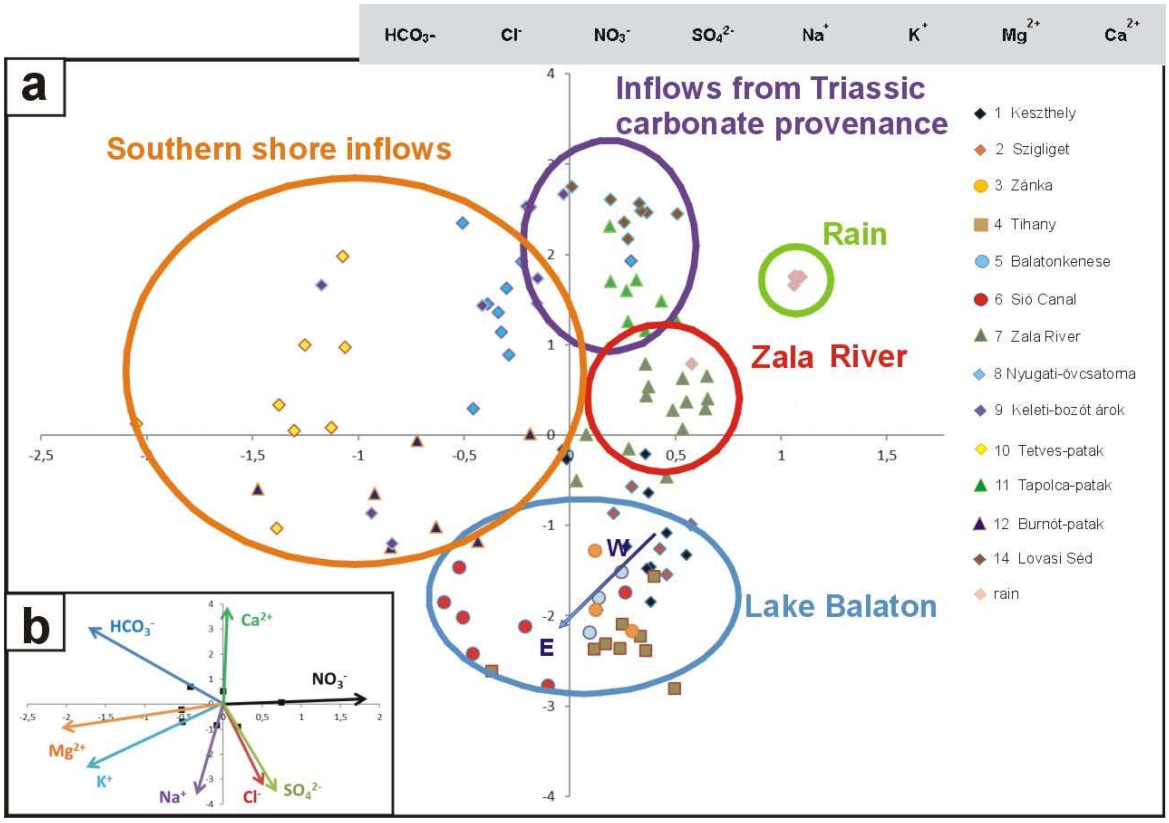

Figure 2 a Cluster analysis of water chemical parameters at the sampling sites in tributaries and Lake Balaton based on concentrations of the ions shown on top of the insert. **b** Selected ion directions in the analysis of multivariate, multidimensional chemical data.

The distribution of tributaries in clusters appeared to correspond primarily to the geology of the provenance: the carbonate-rich catchment area of some north shore inflows separated from the other smaller tributaries arriving from mixed geological terrain, whereas the Zala River was distinct from all other streams.

2.3. TSM per unit volume in tributaries

The amount of incoming solid material per unit volume of water was estimated by measuring the mass of filtered particles (in g m^{-3}) in all major and some smaller tributaries. Water discharge showed large variations, both annually (the total discharge by tributaries into Lake Balaton was 174, 120 and 193 m^3 s^{-1} in 2016, 2017 and 2018, respectively) and seasonally, particularly for the smaller streams. Nevertheless, each stream was sampled 12 times and the

Zala river 23 times over a two-year period, and both normal and high-water conditions were encountered, so we chose to take the average of the values of measured total suspended matter (TSM) per unit volume of water for each watercourse. The average amount of TSM over the sampled two-year period varied between 3.9 and 11.9 g m^{-3} for the 12 sampled inflows. Only three tributaries were responsible for more than 90% of the water discharge into the lake, making these inflows the largest suppliers of allochtonous minerals to the lake. Zala river, Nyugati-övcsatorna and Keleti-Bozót-árok were characterized by 3.9, 4.8 and 7.4 g m^{-3} average TSM values, respectively. The relatively smaller load of TSM per unit volume carried by the Zala river likely resulted from the deposition of a significant fraction of solid material in the Kis-Balaton reservoir, a semi-natural swamp that the Zala flows through before entering the lake.

2.4. Morphologies and sizes of carbonates (detrital vs. precipitated)

Lakewater chemistry is responsible for some of the differences in the properties of allochtonous and autochtonous carbonate minerals of the sediment.

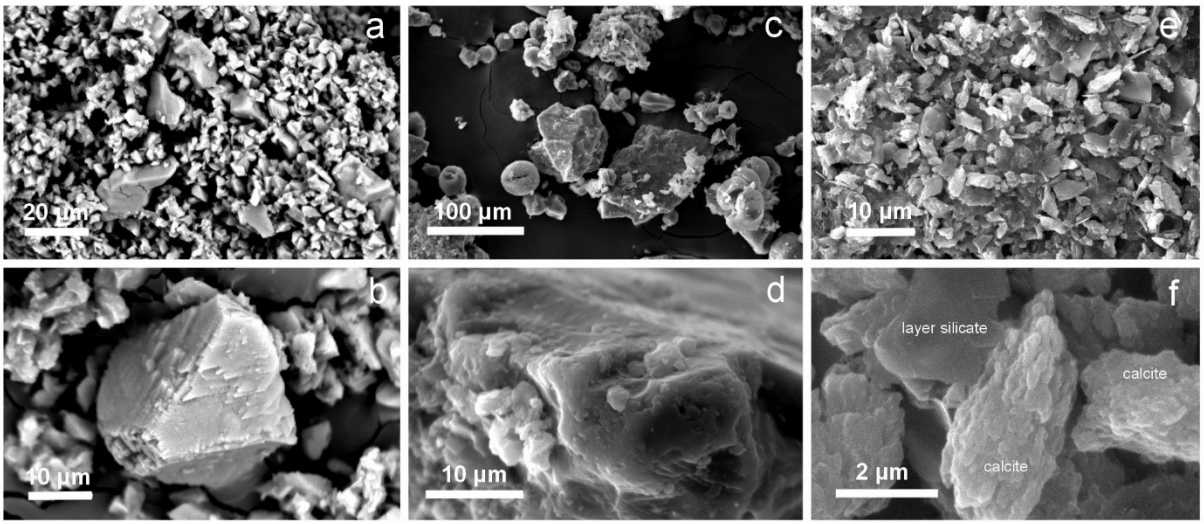

Figure 3 Secondary electron SEM images of typical mineral particles filtered from stream, rain and lakewater. (Note the different length scales of the images.) **a.** Tributary-originated mineral grains with various sizes (small particles are calcite and clay minerals, large ones are quartz crystals). **b.** A weathered calcite particle from Lovasi Séd stream. **c.** Large quartz grains, pollen and unidentified mineral particles from a rainwater sample. **d.** A characteristic quartz particle with a wind-eroded surface. **e and f** Mg-bearing calcite particles that precipitated from lakewater and allochtonous sheet silicates from a lakewater sample; the morphologies and sizes of aggregate-looking, elongated Mg-bearing calcite crystals are typical for particles precipitated from Lake Balaton.

Allochtonous carbonate particles from distinct sources (carried by tributaries and dry or wet deposited from the atmosphere) have similar mineralogies as the lake sediment, since both contain calcite and dolomite. However, detrital carbonate particles were found mostly in large grains (several tens of µm), and typically with euhedral morphologies (Fig. 3a – d). In contrast, silt-sized particles that make up the lake sediments (Fig. 3e) were found to be dominated by low-magnesian calcite with a distinct, elongated, aggregate-looking morphology and a rather constrained particle size (Fig. 3f) between about 2 and 8 µm (Nyirő-Kósa et al., 2018). In addition, their compositions and, consequently, the cell parameters of autochtonous carbonates distinguish them from their detrital counterparts.

2.5. Mg content of calcite and dolomite from XRD

Shifts in the values of cell parameters of calcite and dolomite, as measured using XRD, have been used for the analysis of their Mg content (Zhang et al., 2010; Tompa et al., 2014). Because of the smaller size of the Mg^{2+} ion relative to Ca^{2+}, its presence in calcite causes a shrinkage of the unit cell; conversely, dolomite with an anomalous, Ca-rich composition has a larger unit cell than stoichiometric dolomite. We measured the d_{104} lattice spacings of both calcite and dolomite in XRD patterns obtained from the suspended material that was filtered from 40-l water samples (Fig. 4).

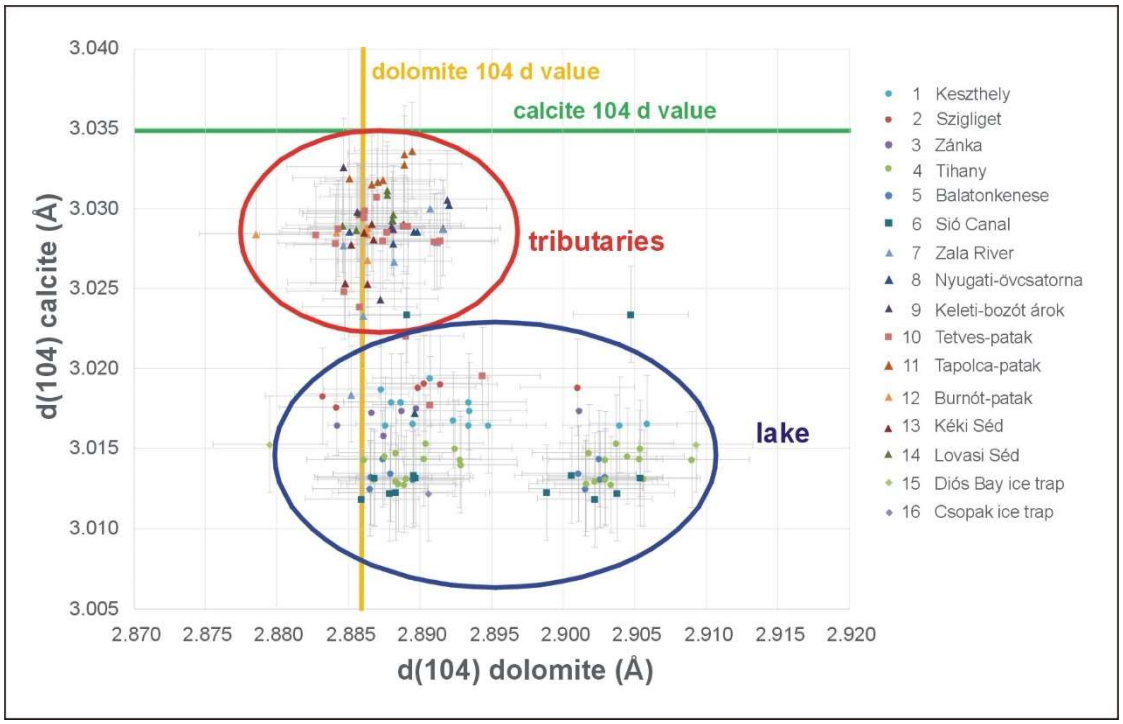

Figure 4 Calcite and dolomite d(-104)-values measured on XRD patterns obtained from suspended particles collected from tributaries, Lake Balaton, and the Sió Canal. Each datapoint represents a sample, except for some samples from the Eastern Basin of the lake, for which the dolomite -104 peak was split and thus two data points correspond to each of these samples (error bars: +/- 0.003 Å). The d(-104)-values of stoichiometric calcite and dolomite are represented by the green and yellow lines, respectively.

Whereas the measured d_{104} values of calcite particles carried by the tributaries suggested a $MgCO_3$ content between 0 and 4 mol%, the same parameter was significantly smaller in calcite from the lake, corresponding to an average Mg content of about 6 to 8 mol% (as calculated using the calibration curve by Zhang et al. (2010)). The difference in the Mg content of calcite types reflected their distinct origins: we assume the streams carried calcite abraded from mostly Triassic rocks (Fig. 1), whereas the suspended calcite particles in the lake represented predominantly autochtonous material that precipitated from the Mg-rich lakewater. Since dolomite was a minor component in our samples, it produced a relatively low-intensity 104 peak in the XRD patterns. Nevertheless, a shift in the position of this peak between different samples was clearly observable. The measured d_{104} lattice spacings scattered around the value for stoichiometric dolomite (2.885 Å) in the samples collected from tributaries. On the other hand, the majority of suspended matter samples collected from the lake, particularly the ones from the Eastern Basin, contained dolomite that produced a split 104 peak in XRD patterns, suggesting the presence of at least two different varieties. One type of dolomite produced d_{104} values close to that of the stoichiometric mineral, presumably

indicating its detrital origin. The other type appeared to be a Ca-rich variant (with a larger d_{104} value), and its presence in the Eastern Basin suggested a relationship between its formation and the higher dissolved Mg/Ca ratio of the water than in the western part of the lake.

2.6. Compositions and structures of precipitated calcite and dolomite

Since XRD provided a bulk, averaged view of the mineralogy of suspended matter, we also used transmission electron microscopy to study the properties of individual carbonate particles. Our observations confirmed the large variation of Mg content in individual Mg-bearing calcite particles and the close association of calcite with nm-scale flakes of the clay mineral smectite, as reported by Nyirő-Kósa et al. (2018). In addition, the anomalous, Ca-rich dolomite fraction identified by XRD could be also characterized using combined information from TEM images, SAED patterns and EDS element maps (Fig. 5).

A group of carbonate particles and a larger diatom fragment are shown in Figure 5a, from a sample collected in a sediment trap in Csopak Eastern Basin) in January 2017. Whereas four of the numbered carbonate particles were Mg-bearing calcite with a Mg/Ca mol ratio of 0.1 or less (Fig. 5e), particles #2 and #6 had very high Mg contents (Mg/Ca = 0.6 in the case of #6 (Fig. 5f). SAED patterns obtained from the same particle #6 (Fig. 5g−h) displayed rows of reflections (marked by arrows in panel h) that suggested at least a partial, dolomite-like ordering of Ca and Mg in its structure. Therefore, we interpret the anomalous dolomite reflections observed in XRD patterns as produced by “dolomite” particles (such as #2 and #6) that have some ordering of Ca and Mg in their structures but are significantly enriched in Ca relative to genuine dolomite (in which Mg/Ca = 1).

In addition to identifying two types of carbonates in the suspended matter, including the dominant low-magnesian calcite and minor Ca-rich “dolomite”, TEM element maps revealed compositional variety even within some single particles. Although we found that low-magnesian calcite with homogeneous composition was the dominant carbonate particle type in suspended matter, both Ca-rich “dolomite” and low-magnesian calcite with a non-uniform Mg distribution appeared to be ubiquitous minor constituents.

3. Importance of atmospheric deposition

The primary goal of the sampling campaign was to quantify and characterize the filterable solid phase of precipitation and to give a measurement-based estimate for the deposited dust. We aimed to quantify the Saharan dust flux of the Carpathian Basin with a special attention to Lake Balaton and its sediment budget. Increasing frequency and intensity of Saharan dust events were reported by previous studies (e.g., Varga et al. 2013, 2014). By identification and sampling of these episodes, we also provide comprehensive characterisation of Central European washout events with regard to synoptic meteorology, mineralogical phase composition and particle size distribution.

3.1. Sampling, amount of precipitation

Rainwater samples were collected in Csopak, about 800 m from the lake, over a year from April 2016 to March 2017. In this period, 74 precipitation events occurred at the sampling location and 46 samples were collected. Based on daily meteorological reports of the Hungarian Meteorological Survey (HMS), from April 2016 to March 2017 the distribution of

precipitation was fairly even geographically over the surface of Lake Balaton (596 and 543 mm in the Eastern and Western Basins, respectively) but highly variable over time. From 46 rain events in Csopak (with precipitation > 3 mm in each case) we measured a total of 393 mm, amounting to 66% of the annual rainfall registered by the HMS for the eastern basin of the lake.

3.2. Origins and distribution of air masses associated with precipitation events

The atmospheric pathways of moisture transport leading to the observed precipitation events were evaluated using a Lagrangian trajectory model. Transport route directions of every precipitation events were determined, 48-hour trajectory simulations of samples were prepared in the ranges of 500–1500 m, 1500–3000 m and 3000–6000 m a.s.l.. The trajectory analyses suggest that the precipitation in Csopak derived from different sources. In the study period, the Atlantic area was the main source region, as 67.8% of the total amount of annual precipitation came from the region. Approximately 16.2% of the annual rainfall derived from the Mediterranean source region, followed by Northern Europe (8.1%) and Eastern Europe (7.9%).

Significant amount of rainfall arrived mainly from the Atlantic sector (west), particularly in summer and autumn, whereas the other three sectors contributed little to the annual precipitation, as is typical in this Central European region. Precipitation events caused by air masses arriving from the Mediterranean deserve special attention, since Saharan dust events (SDE) are known to deliver significant amount of solid material to the region (Varga 2020). SDE transport was identified by modeling 72-hour trajectories for air masses arriving from the south. As a result, five individual SDE events were detected in the sampling period, three in spring (with 4, 55 and 3 mm rain recorded), one in summer (9 mm), and one in autumn (5 mm).

3.3. Meteorological background of Saharan dust events and dust transport

1. Saharan dust episode/ SDE_1: 08 April 2016.

A low-pressure system formed over northern Africa (Algeria), at the lee side of the Atlas Mountains on 05. April 2016 (Fig. 5). According to the visibility-reducing surface weather reports of the Naval Research Laboratory, intense dust storms were developed in the next days also in the central and northern regions of Lybia. The dust-loaded airmass was clearly visible over Gulf of Sidra and Cyrenaica on MODIS images of NASA's Aqua and Terra satellites. Airmasses with elevated dust concentration reached the Carpathian Basin at the foreside of the (north) eastward-moving shallow cyclone.

2. Saharan dust episode/ SDE_2: 11/12 May 2016.

In early May, intense dust storms were reported from the intramontane basins, foreland and Chott regions of the Atlas Mountains by the surface observations and very high dust concentrations were observed over the western and central basins of the Mediterranean region for several days. As a result of the strong meridional flow coupled to this situation, on 11–12 May 2016, precipitation with a large amount of Saharan dust fell again in the territory of Central Europe. On the front of a shallow, then increasingly deepening low-pressure atmospheric centre formed over SW Europe and NW Africa. The steep pressure gradient between the cyclonal system and the static high-pressure regions over the Sahara led to the strong southerly airflow.

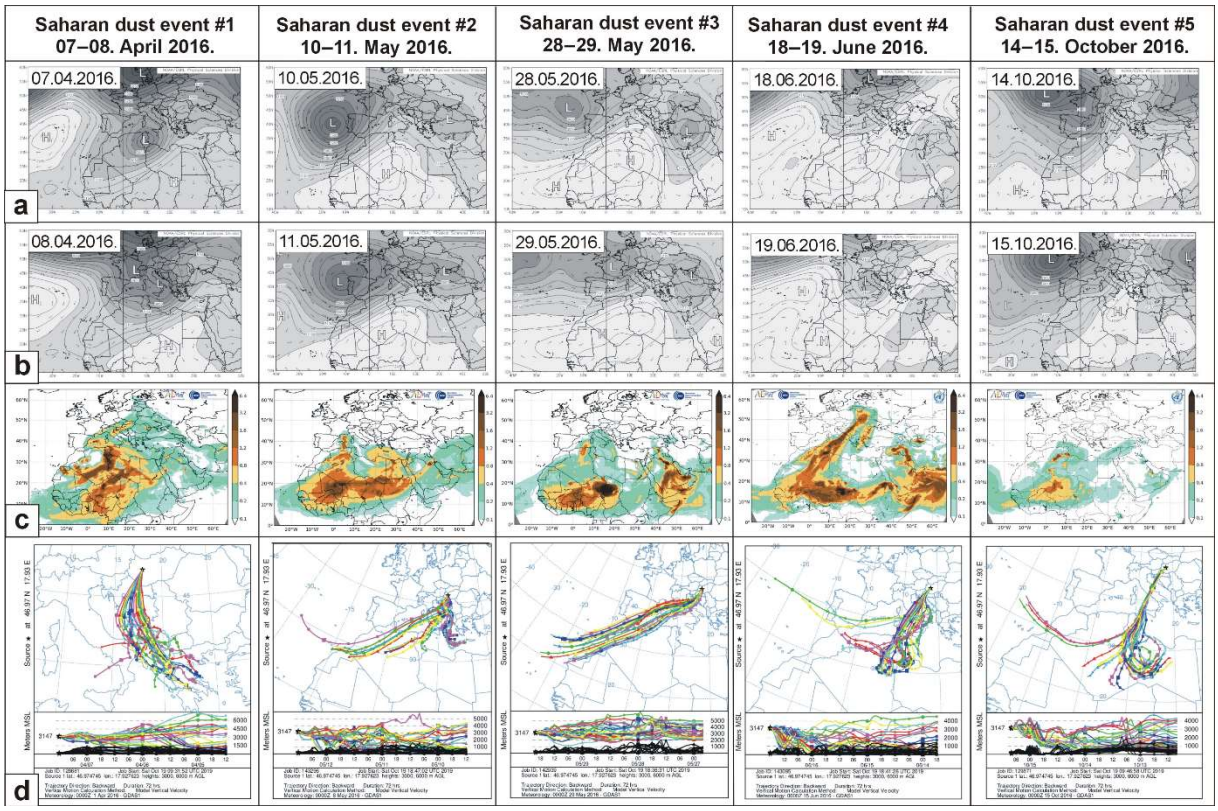

Figure 5 a–b Synoptic meteorological background (mean geopotential height map and wind vectors at 700 hPa; **c** Modelled dust loading (NNMB/BSC); **d** 72 hours HYSPLIT model of the examined Saharan dust depositional events in the range of 3000–6000 meters.

3. Saharan dust episode/ SDE_3: 29 May 2016.

In late May, another dust washout episode was observed in Hungary, the synoptic background was similar to the SDE #2; SW flow dominated the study area as a result of the pressure difference of an eastward propagating cyclone and the African high-pressure belt. The intramontane basins of Atlas were obscured by the dust storms, while areas of Chott Melrhir and Felrhir were also affected by the strong winds, the presence of dust confirmed by local observations in Hungary.

4. Saharan dust episode/ SDE_4: 19 June 2016.

Rainfall on 19 June 2016 contained Saharan dust, which was well visible on car windshields and rain-exposed landmarks. The strongest south-western flow occurred between the high-pressure region from the north-west of the African continent to the Balkans and the undulating frontal zone bisecting Europe, which was later followed by an Italian-centered vortex. The source of the dust was the southern foreland of the Atlas.

5. Saharan dust episode/ SDE_5: 15 October 2016.

An autumn dust episode was also identified in 2016, on 15 October rainfall washed out a large amount of Saharan dust in the western part of Hungary. An extensive cyclone over Western Europe and its SW flow determined the synoptic situation of these days. A high-pressure blocking zone over the Central Mediterranean led to strong meridional winds on the warm sector of the low-pressure system carrying mineral dust from the Tunisian dry salt lakes (Chott Melrhir and Chott Jerid) to Central Europe.

3.4. Particle size characteristics of the Saharan dust samples

A total of 50,000 individual dust particles by samples were scanned. Due to the presence of aggregated and non-mineral (e.g. pollens, plant fragments), irregularly shaped particles an additional mathematical filtering was applied. The exclusion rule was based on low (<0.65) circularity and convexity scores. Still, a few giant, irregular particles remained in the dataset, which caused an additional coarse-grained mode on the calculated grain size distributions. This bimodal character was transformed into a unimodal one by parametric curve fitting. Two Weibull-distributions were fitted on the grain size distributions (by an iterative numerical method as a least-square problem to assess the appropriate goodness of fit of measured data and calculated size distributions of constructed subpopulations). The fine-grained subpopulations were identified as the Saharan dust cluster, while the coarse population was dominated by aggregated particles and irregularly shaped objects (e.g. plant fragments, most likely from below cloud scavenging). However, the exclusion of a few giant particles of Saharan origin cannot be ruled out, either.

The volume-based mean diameter of the identified Saharan dust particles fell into the range between 20 and 80 µm, with modal values ranging from 30 to 50 µm (Fig. 6).

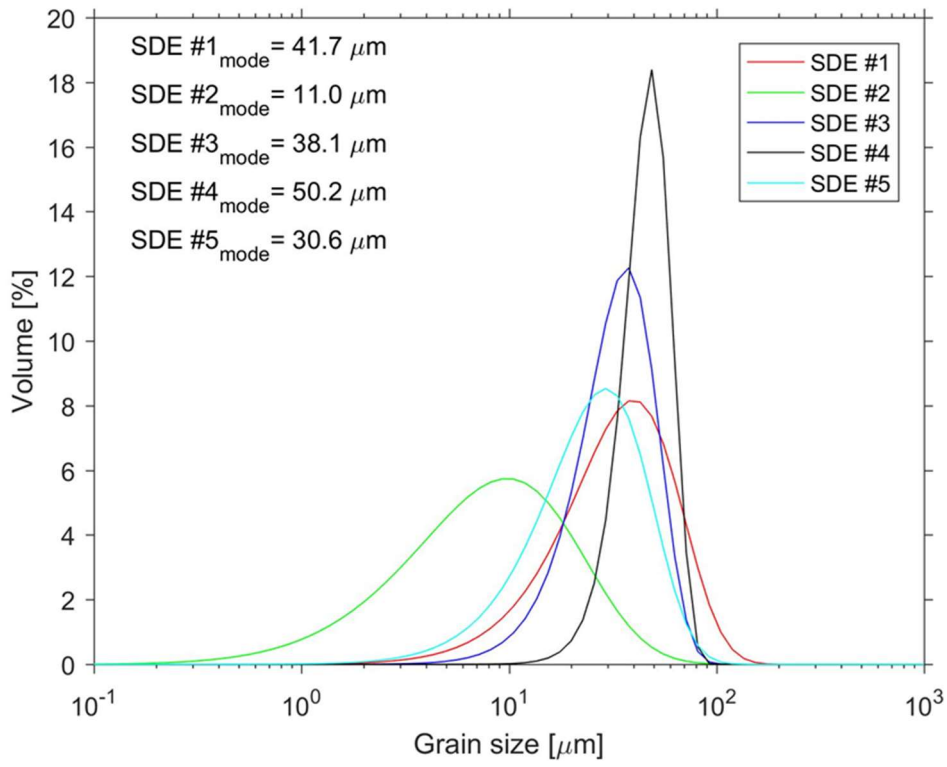

Figure 6 Volume-based mean diameter of the identified Saharan dust particles.

Only the SDE #2 sample was dominated by significantly smaller particles (modal value ~11 µm). The shapes of the particles were rather similar in all individual events, with the exception of particles in the SDE#2 sample. As a result of the large volumetric amount of fine-grained fractions in this sample, the grain shape parameters were higher (partly due to the applied magnification, partly because of the less irregular shapes of fine silt particles).

A first draft of the paper with the above results has been prepared and will be submitted this year (paper #1).

4. Mineral budget of Lake Balaton

We focused most of our efforts on identifying the mineral phases in Lake Balaton derived from different sources (provenance, in-situ formation, and atmospheric deposition). The analysis of water chemistry and examination of the morphologies of allochtonous minerals, in particular the types (compositions, particle sizes and habits) of detrital calcite and dolomite, help better understand the effects of catchment mineralogy and sediment formation in the lake.

4.1. Solid material delivered by tributaries over a year

The total amount of suspended matter delivered by tributaries into the lake was estimated by multiplying the measured average TSM per unit volume for each stream with the annual water discharge of the stream, as reported by the Central Transdanubian Water Directorate (CTWD), and then adding the mass of material carried by all streams. Since we did not sample some of the small tributaries (many of which are ephemeral), we applied correction factors for the total water discharge. The CTWD divides the lake into four parts from West to East (I Keszthely Basin, II Szigliget Basin, III Zánka Basin and IV Eastern/Kenese Basin), and reports the total water discharge for each basin annually. The watercourses we sampled contribute close to 100% of the reported discharge into Basin I, 60% into Basin II, 30% into Basin III and only 14% into Basin IV. Therefore, we multiplied the measured annual TSM mass with 1, 1.7, 3.5 and 7.1 for Basins I, II, III and IV, respectively. Since the vast majority of water input arrived in Basins I and II, and the amount of TSM delivered into Basins III and IV was almost negligible, this procedure was assumed to carry a relatively small error. In summary, annual mass of TSM delivered by tributaries was calculated as 24,000 t y^{-1}, with most of the material arriving into Basin I (11,000 t y^{-1}) and Basin II (10,000 t y^{-1}).

4.2. Dust deposition

Dry deposition of atmospheric particles also contributes to the mineral budget of Lake Balaton. Annual concentrations of deposited dust were measured by the National Air Pollution Measurement Network at several locations around the lake until 2007, and only in Siófok after 2007. Dust from distant sources, including incursions of air masses originating in the Sahara are known to deliver significant amount of dust to the region, typically in springtime (Borbély-Kiss 2004). However, in the lack of seasonally resolved data it was impossible to identify the effects of remote and local sources. As seen from the data reported for the years before 2007, there were significant differences in the measured concentrations among the individual locations, in some years reaching a factor of 4 between the lowest and highest values. Apparently, local sources from construction, agriculture and traffic might have strongly affected the amount of deposited dust, limiting the accuracy of any estimation of total dust deposition. Based on the average of all available data for the period from 2003 to 2017, we estimated a total of 33,000 t y^{-1} dry deposition directly onto the lake surface, a value about 16 times larger than the amount of solid material delivered by precipitation.

4.3. Solid material in precipitation

The amount of filtered solid materials at each rain event varied from below detection limit to 0.24 g m^{-2}. While transport from the Atlantic sector resulted in most of the collected precipitation (73% of the total), these events delivered only 58% of the measured TSM. In contrast, three of the five identified SAD events delivered a large amount solid material. Thus,

compared to their contribution to the annual precipitation, SAD events delivered a disproportionately large amount of allochtonous minerals into the lake. Annual deposition rate of Saharan dust at the site was found to be in the order of 0.5 g m^{-2} $year^{-1}$. We studied the mineralogy of solid material collected during the SAD event of April 8, 2016 by using SEM and XRD. The sample was dominated by common rock-forming minerals, including clays, quartz, feldspars and dolomite. Based on our year-long rain collection, an upper limit of 2100 t y^{-1} of solid matter delivered by precipitation to the lake can be assumed.

4.4. Mass of precipitating carbonate

The mass of annually precipitating carbonate can be estimated in at least three different ways, all of which produce rather inaccurate results.

(1) The average thickness of Holocene lake sediments is about 6 m, deposited over 15 thousand years (Cserny & Hertelendi 1995). If we consider 2/3 of this sediment consisting of autochtonous carbonate minerals, then an annual increment of 0.27 mm pure carbonate amounts to about 436,000 t a^{-1} (calculating with the density of pure calcite). Of course, this figure does not take into account variations in the intensity of carbonate precipitation over time.

(2) Another way of estimating annual carbonate precipitation is to consider the balance of dissolved Ca and Mg arriving through tributaries and rain; and leaving through the Sió canal, and assuming that the difference constitutes the precipitated material (with the composition of lakewater being approximately constant over the residence time of water. The balance of HCO_3^- is not considered, since its concentration is affected by the dissolution of atmospheric CO_2). By using our measured water chemistry data for tributaries, rain and the Sió Canal, and taking an average water balance of the 5 years from 2014 to 2018 (the residence time of lakewater is 4.7 years; Kutics, 2019), we calculated about 8.3E+9 mol Ca^{2+} and 7.8E+9 mol Mg^{2+} "remaining" in the lake annually. These values convert to nearly 1.5 million tonnes of dolomite with a Ca-rich composition of $Ca_{0.52}Mg_{0.48}CO_3$, equivalent to 0.88 mm consolidated sediment thickness, which is more than three times the amount calculated from the total sediment thickness (0.27 mm).

(3) Measuring the amount of suspended material in the lake may appear the most direct way of estimating the mass of precipitating carbonate minerals. However, this approach is also loaded with uncertainties, particularly in the case of Lake Balaton. Sediments in the shallow lake are prone to resuspension by turbulence resulting from even relatively gentle winds, thereby mixing freshly precipitated and older carbonate particles. Moreover, the intensity of carbonate precipitation is highly heterogeneous both spatially and temporally (e.g. phytoplankton blooms can result in "whitening" events), making point measurements hardly representative. In our 66 samples the mass of total suspended matter (TSM) ranged between 3.81 and 50.20 g m^{-3}. The average mass of TSM measured in the Western Basin (17.85 g m^{-3}) is significantly higher than in the Eastern Basin (8.41 g m^{-3}), probably due to the fact that the eastern part of the lake is deeper. Material in the Sió canal is less affected by resuspension, and is characterized by an average TSM mass concentration of 6.11 g m^{-3}. As expected, high wind speeds result in larger amounts of TSM, although there is significant variation in the measured TSM mass between different parts of the lake. We assumed that the sample taken on 12th September 2018, when a 3-day calm period preceded our sampling, did not contain much resuspended sediment and was thus the most representative for freshly precipitated carbonate. On this day we measured 5.68 g m^{-3} TSM in the Western and 5.56 g m^{-3} in the Eastern Basin. Based on Stokes' law, calcite grains with a diameter of 5 μm need 3 days to

settle 3 m, whereas grains of 2 μm size need a week. On this basis, it was considered that the amount of suspended material measured in the water sample of 12th September 2018 represented freshly precipitated calcite formed in about 3 days. Based on this figure and assuming constant calcite precipitation over a year, annually about 1.3 million t carbonate forms in the lake, producing a layer of 0.76 mm thickness.

A first draft of the paper with the above results has been prepared and will be submitted this year (paper #2).

Altough this project formally terminated, the research will be continued and more papers are expected to be submitted in the coming years. The list of published and anticipated papers can be found below.

Publication activities

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** Rostási, Á., Topa, B. A., Weiszburg, G.T., Gresina, F., Gelencsér, A., Varga, G. (2021) Increased number of intense Saharan dust episodes in Central Europe – Was 2016 an exceptional year or this is the new normal? WEATHER AND CLIMATE EXTREMES

***#2** Rostási, Á., Rácz, K., Fodor, M., Topa, B., Molnár, Z., Weiszburg, T.G., Pósfai, M. (2021) Pathways of carbonate sediment accumulation in a large, shallow lake. SEDIMENTOLOGY

Varga, G., Roettig, CB., Dagsson-Waldhauserova, P., Gresina, F., Rostási, Á., Kovács, J. (2021) Identification and granulometric characterization of (giant) Saharan dust in sedimentary units (abstract ID: 8287) Goldschmidt 2021 Conference (Lyon, France 4–9 July)

Pósfai, M., Molnár, Z., Pekker, P., Rácz, K., Rostási, Á., Dódony, I., Pálfi, I., Magyari, E., Istvánovics, V. (2020) Ásványképződés a Balatonban: karbonátok kiválása, átalakulása és esetleges szerepe az algavirágzásban. „A Balaton kutatása Lóczy Lajos nyomdokán – könyvbemutatóval egybekötött emlékülés Lóczy Lajos halálának centenáriumán" MTA Magyar Tudomány Ünnepe rendezvény, Budapest, 2020.11.11.

Rostási, Á., Fodor, M., Rácz, K., Topa, B., Weiszburg, T., Pósfai, M. (2019) A Balaton üledékképződésének ásványmérlege. poszter, Földtani és Geofizikai Vándorgyűlés, Balatonfüred, 2019. október 3−5.

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Pósfai, M., Molnár, Z., Rostási, Á., Fodor, M., Cserny, T. (2019) A Balaton üledékének kutatása. Budai T., Palotás K. Piros O. (szerk.) Földtani és Geofizikai Vándorgyűlés. Magyarhoni Földtani Társulat és Magyar Geofizikusok Egyesülete, Balatonfüred, 16−19.

Pósfai, M., Fodor, M., Rostási, Á., Molnár, Z., Váczi, T., Ható, Z., Kristóf, T. (2018) The role of clays in the heterogeneous nucleation of carbonates. Goldschmidt Conference on Geochemistry, Boston, 2018. August 12−17.

Molnár, Z., Váczi, T., Rostási, Á., Pósfai, M. (2018) Simulation of the heterogenous nucleation of Mg-bearing calcite from Lake Balaton under controlled conditions. Meeting of Young Geoscientists. 2018.04.06–04.07. Hajdúszoboszló, 57–58.

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Rostási, Á., Molnár, Z., Fodor, M., Bereczk-Tompa, É., Váczi, T., Pósfai, M. (2017) Templated nucleation and growth of calcite in a freshwater environment. Goldschmidt Conference 2017. 08. 13−18. Paris, France - oral presentation (Abstract ID: gold2017:abs:2017005820)

Pósfai, M., Rostási, Á., Topa, B., Molnár, Z., Nyirő-Kósa, I., Bereczk-Tompa, É., Fodor, M., Cora, I., Kovács, A., Váczi, T., Weiszburg, T., Haas, J. (2017) Karbonátásványok kiválása a Balatonban. in Dégi, J., Király, E., Kónya, P., Kovács, I., Pál-Molnár, E., Thamóné, B.E., Török, K., Udvardi, B. (szerk.) Ahol az elemek találkoznak: víz, föld és tűz határán: 8. Kőzettani és Geokémiai Vándorgyűlés Budapest, Magyarország, Magyar Földtani és Geofizikai Intézet (2017) 205 p., 143–146.

Pósfai, M., Nyirő-Kósa, I., Rostási, Á., Bereck-Tompa, É., Cora, I., Koblar, M., Kovács, A. (2016) Nucleation, morphology, structure and composition of Mg-calcite, the dominant mineral in the mud of Lake Balaton Paper: DOI: 10.1002/9783527808465.EMC2016.5814 (2016) The 16th European Microscope Congress, Lyon, 29.08.– 02.09.2016.

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Pósfai, M., Nyirő-Kósa, I., Rostási, Á., Bereck-Tompa, É., Cora, I., Koblar, M., Kovács, A (2016) Mg-calcite formation in a freshwater environment (Lake Balaton): nucleation, growth, structure and composition. European Microscopy Congress 2016: Proceedings, Wiley-VCH Verlag GmbH & Co. KGaA, 1176 –1177.

*Planned papers have tentative titles. Additional studies may also result, but at this point these two papers are in a sufficiently advanced state to be cited here.

General comments, further collaborations, scientific plans

The scientific report summarizes the results related to the objectives detailed in the research plan for the period from 1 October 2016 to 30 September 2020 with a 12-month-adjournment in 2017 (maternity leave).

Collaborations and laboratory experiments planned for the final phase of the project were strongly influenced by the COVID–19 pandemic situation. The emergency state necessitated overriding previous plans. Some of the examinations were delayed (e.g. size distribution measurements of Saharan rain samples) and a conference participation had to be rescheduled after the finishing deadline.

In this project we produced new scientific results along the following lines:

- based on modeling the nucleation of carbonate species by laboratory experiments we found that the presence of smectite promotes calcite precipitation;
- we identified the morphology of Mg-bearing calcite and clarified the conditions of its formation in Lake Balaton;
- features of atmospheric deposition associated with Saharan dust events were characterized;
- with a synthesis of incoming phases from different sources, precipitation in the water body and deposition, we set up a preliminary mineral budget for sedimentation in Lake Balaton.

The research highlights several other scientific collaborations:

1. A permanent Saharan dust monitoring program is running in the Research Centre for Astronomy and Earth Sciences. Combined application of satellite-borne aerosol products, numerical simulations, meteorological analyses and surface observation reports allowed the compilation of a more than 40-year long time series of dust events identified in the Carpathian Basin. Based on the collaboration with György Varga we propose a new OTKA research project entitled “Giant Saharan dust in Europe: changing climate or uncertain analyses?” with two major objectives. The first objective is to provide a direct and accurate particle characterization method and to create a granulometric database of Saharan dust deposited in Europe to provide reliable data on particle size and shape. The second objective is to acquire observational understanding of African dust transport and deposition into Europe. Specifically, we will utilize an improved dust episode identification method completed with CALIOP measurements (supplemented by MODIS, MISR, and IASI observations of dust) to characterize the three-dimensional features of Saharan dust transport towards Europe.
2. Based on my scientific activities András Gelencsér, head of the MTA–PE Air Chemistry Research Group f (RGAC), invited me to join RGAC. I started the work with the goal of identifying transport pathways for specific particle types and of estimate the mass of deposited dust in Hungary.
3. According to the results of recent studies, the intensity of the photoinduced luminescence of water is dramatically increased by the presence of policyclic aromatic hydrocarbons (PAHs) at concentrations as low as ppb (where it could not originate from the own photoluminescence of these compound). Hence, such luminescence investigations of rainwater samples may provide useful pieces of information regarding their PAH contamination, even at a very low level. New laboratory

experiments are performed in collaboration with Ottó Horváth and Lajos Fodor (Research Group of Inorganic Chemistry, University of Pannonia).

4. A new line of the research developed by the quantitative and qualitative analysis of microplastic particles from rainwater in collaboration with Norbert Miskolczi (head of Department of MOL Hydrocarbon and Coal Processing, University of Pannonia).

The project produce results along above lines that will warrant the publication of papers on other topics as well.

Overall, the project helped me greatly in the last three years to perform a complex research. I am grateful to the reviewers for their useful comments and the administrative personnel of NKFIH for their work.

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