

Distribution and composition of Mg-calcite and dolomite in the water and sediments of Lake Balaton

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Lake Balaton is a large and shallow lake that is of great economic and cultural importance in landlocked Hungary. Even though the lake has been studied extensively in the last century from a large number of scientific aspects, the mineralogy of its sediments has not been fully explored. The mud at the bottom of the lake consists mostly of silt-sized grains of carbonate minerals with compositions between those of calcite (CaCO_3) and dolomite $\text{CaMg}(\text{CO}_3)_2$. In order to understand the processes of carbonate precipitation and the influence of water budget fluctuations on the mineralogical character of the sediment, we used X-ray powder diffraction to analyze the changes of cell parameters of carbonate minerals in the upper half meter of the sediment. The major carbonate phase is Mg-calcite that shows a distinct reduction in cell parameters from west to east, reflecting an increase of its Mg-content, in parallel with a gradient of dissolved Mg/Ca ratio in the water. Intriguingly, dolomite, the other widespread carbonate phase in the sediment, also shows a change in cell parameters from west to east, with the deviations from values of stoichiometric dolomite being largest in the Eastern Basin of the lake. The similar pattern of cell parameter changes of Mg-calcite and dolomite suggests that ordered dolomite with slightly anomalous, Ca-rich composition also forms in the lake, probably by direct precipitation from the water. In contrast, protodolomite forms within the sediment through diagenetic processes. Based on our X-ray powder diffraction measurements, we propose a model of carbonate mineral formation and transformation in Lake Balaton. Since the Mg/Ca ratio of the water appears to be the major factor in controlling the compositions of carbonate minerals, and this ratio in turn is governed by the amount of water supply, the properties of the precipitating carbonate minerals are affected by the actual level of the lake water.

Key words: Lake Balaton, sediment mineralogy, Mg-calcite, dolomite, protodolomite

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Introduction

The precipitation of carbonate minerals in hard-water lakes is a common phenomenon that affects both sediment formation and nutrient cycles (Talbot 1990). The formation of suspended, silt and clay-sized solid particles affects the optical properties of the water, limiting light availability for photosynthesis, and influences the metabolism of filtering organisms such as mussels and some zooplankton species (G.-Tóth 1992). Carbonate minerals also exert some control over the availability of nutrients, including phosphorous (Herodek and Istvánovics 1986), through co-precipitation or surface adsorption (Istvánovics et al. 1989; Hartley et al. 1997), and the sediment is an important source of nitrogen as well (Présing et al. 2001). Thus, the mineralogical character, such as grain size, composition and structure of the carbonate minerals is of interest for an assessment of their ecological impact. On the other hand, some crystal chemical characteristics of sediment minerals can be used as proxies for past changes in water chemistry (Gierlowski-Kordesch 2010). In this study we analyze the structures of carbonate minerals that precipitate in Lake Balaton and discuss the environmental implications of the variable Mg contents of both calcite and dolomite.

Lake Balaton is a large (590 km² surface area), shallow (~3.5 m on average) lake in Western Hungary (Fig. 1). Although the long axis of the lake is approxi-

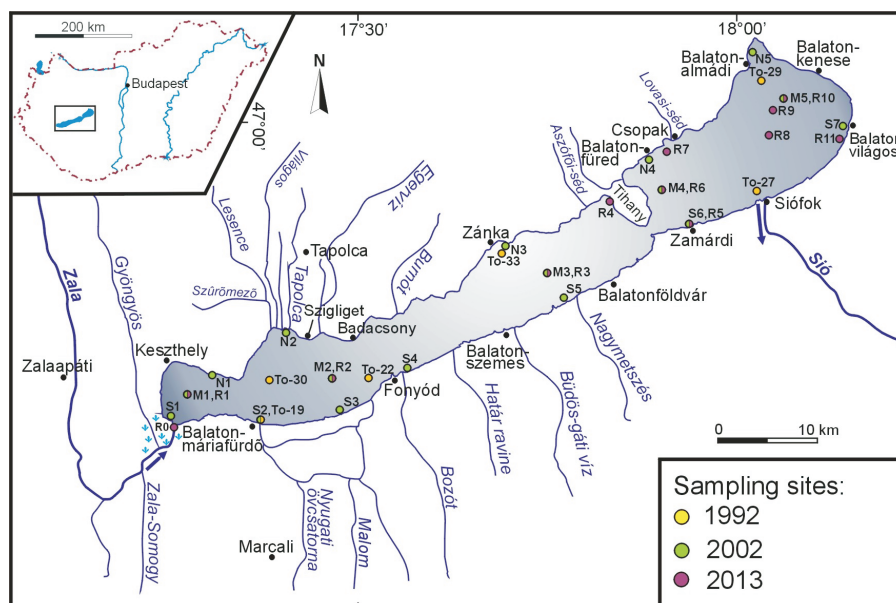


Fig. 1
Map of sampling locations. ‘R’ marks locations where we collected sediment and suspended particles in 2013. ‘N’, ‘M’ and ‘S’ mark places where sediment samples were collected by Hlavay and coworkers in 2002, and ‘To’ denotes the locations from which we used samples from drillings performed by Cserny and coworkers in 1992

mately parallel to the SW–NE direction, in this paper we adopt the terms that are used in common language, and refer to the W–E and N–S directions as the long and short axes of the lake, respectively. The Tihany Peninsula divides the lake into the Western and Eastern Basins. The Zala River, which carries between half and two-thirds of the annual inflow, enters the lake at its westernmost end. Other important tributaries, such as the Nyugati-övesatorna and streams near Szigliget also enter the lake at its western end, while the only (artificial and temporary) outflow, the Sió Canal, drains the lake near its eastern end. As a result, the lake water is typically characterized by chemical gradients from W to E, affecting the composition of particles that precipitate from the water (Müller and Wagner 1978; Tullner and Cserny 2003). Strong winds and the resulting turbulence stir up the upper layer of the sediment, and redeposit the suspended material. The predominantly northerly winds and the consequent wave action result in the accumulation of coarse-grained sediments along the south shore (Lóczy 1913; Cserny 1987; Máté 1987).

Since the geology of the catchment area of Lake Balaton is dominated by carbonate-rich rocks such as limestone, dolomite and clastic sedimentary rocks, the water is characterized by high concentrations of dissolved HCO_3^- , Mg^{2+} and Ca^{2+} . As a result, the Holocene sediments of Lake Balaton are predominantly calcareous (Lóczy 1913), consisting mostly of silt-sized grains of carbonate minerals (Müller and Wagner 1978; Cserny et al. 1991; Tullner and Cserny 2003). Detrital calcite and dolomite, as well as both authigenic and biogenic aragonite (from mollusk shells) (Bidló 1960) are present in the sediment. However, the most abundant sediment mineral is Mg-calcite that precipitates from the water (Müller and Wagner 1978; Cserny et al. 1991). In addition to the detrital and primary carbonates, diagenetic “protodolomite” was described (Müller 1970) and later confirmed (Cserny et al. 1991) in the deeper layers of the sediment. The term “protodolomite” does not refer to a valid mineral species but is used to describe a metastable phase with a dolomite-like composition and a presumably partially ordered arrangement of Mg and Ca in its structure (Gaines 1977). The presence of protodolomite raises the question of whether dolomite also forms in the lake. The potential formation of dolomite is intriguing because of the well-known “dolomite problem”, the failure to produce stoichiometric dolomite in the laboratory under temperature and pressure conditions typical of sedimentary environments (Land 1998).

Concerning the compositions and structures of the carbonate minerals, an approximately linear relationship was found between the Mg/Ca ratio in the lake water and the Mg content in the calcite that precipitates from the water (Müller and Wagner 1978). Since the water chemistry is mainly determined by the changing amounts of water supply, the low and high-Mg conditions reflect the alternation of humid and dry periods in the history of the lake, respectively (Tullner and Cserny 2003). Such variations in the local climate over the last three thousand years were also confirmed by studies on the stable isotopic compositions of bi-

valve shells (Schöll-Barna 2011; Schöll-Barna et al. 2012). Thus, the composition of the Mg-calcite that precipitates from the water and is deposited into the sediments of Lake Balaton is apparently related to significant variations of the water level, caused by the alternation of humid and dry climatic periods. However, in the last three centuries anthropogenic influences often overprinted the natural fluctuations of the water level (Zlinszky and Timár 2013).

We were interested in present-day sediment formation processes and wished to understand whether the weather extremes that have sharply increased in their frequency over the last 20 years (Gácsér and Molnár 2013) have measurable effects on the compositions and structures of carbonate minerals that precipitate in the lake. Therefore, we studied sediment samples from the upper 50 cm of the mud and also collected suspended particles from the water. Although the mineralogy of the sediment cores is complex and could be analyzed for a large number of sediment-forming factors, the focus of our present study is on the structures of carbonate minerals that presumably precipitate from the water. By using X-ray powder diffraction (XRD), we determined variations in the cell parameters of calcite and dolomite, and used these data to infer the compositions of these minerals. The results were then used to interpret the processes that lead to the direct precipitation of carbonates, and to analyze the relationships between lake water chemistry and sediment composition.

sediment

Samples and methods

Data from four sets of samples were used in this study: (1) sediment samples and (2) filtered, suspended material collected in the spring of 2013; (3) sediment samples collected in 2002 by Hlavay and coworkers (Hlavay and Polyák 2002); and (4) sediment cores cut in the 1990s (Cserny 2002). Our purpose in using the data from earlier sampling campaigns was to improve the statistics of our data, identify potential changes in sediment formation within the last ten years and to compare the structural features of carbonate minerals occurring near the surface and within the deeper layers of the sediments.

On April 17, 2013 we collected 50 cm-long sediment cores at 11 sites in the lake (samples marked R in Table 1 and Fig. 1). Since the depth of the water was less than 5 m at every location, the sampling was done manually, by pressing a plastic tube of 8 cm diameter into the mud. The sediment cores were divided into 10-cm cylindrical sections the day after sampling, cut in half and dried in air at room temperature. XRD patterns were obtained from material taken from the central parts of the 10-cm core sections. Since some of the cores were shorter than 50 cm, a total of 38 XRD patterns resulted from these samples.

In order to obtain particulate material directly from the water, at the time of the April 17, 2013 sampling, we also collected 40-liter water samples at 5 locations (samples marked RF in Table 1). The samples were decanted and the remaining material filtered using a 0.45 mm Pall GN-6 Metrical Membrane Filter, then dried

Table 1
List of samples used in this study

Locality on shore	Position relative to long axis of lake	Depth from sediment surface (cm)	Sample identifier	Locality on shore	Position relative to long axis of lake	Depth from sediment surface (cm)	Sample identifier
Sediment cores collected in 2002:				Sediment cores collected in 2013:			
Fenépuszta	South	0–10	S1/1	Keszthely	Middle	0–10	R1/1
		10–20	S1/2			10–20	R1/2
		20–30	S1/3			20–30	R1/3
		30–40	S1/4			30–40	R1/4
Keszthely	Middle	0–10	M1/1			40–50	R1/5
		20–30	M1/3	Szigliget	Middle	0–10	R2/1
		30–40	M1/4			10–20	R2/2
		40–50	M1/5			20–30	R2/3
Gyenesdiás	North	0–10	N1/1			30–40	R2/4
		10–20	N1/2	Zánka	Middle	0–10	R3/1
Balaton-máriafürdő	South	0–10	S2/1			10–20	R3/2
		10–20	S2/2			20–30	R3/3
		20–30	S2/3	Sajkod	North	0–10	R4/1
		30–40	S2/4			10–20	R4/2
Szigliget	North	10–20	N2/2	Zamárdi	South	0–10	R5/1
		20–30	N2/3			10–20	R5/2
		30–40	N2/4			20–30	R5/3
		40–50	N2/5			30–40	R5/4
Szigliget	Middle	0–10	M2/1		Tihany	0–10	R6/1
		10–20	M2/2			10–20	R6/2
		20–30	M2/3			20–30	R6/3
		30–40	M2/4			30–40	R6/4
		40–50	M2/5	Csopak	North	0–10	R7/1
Balaton-fenyves	South	50–60	M2/6			10–20	R7/2
		0–10	S3/1			20–30	R7/3
		10–20	S3/2			30–40	R7/4
		20–30	S3/3	Sóstó	Middle	0–10	R8/1
		30–40	S3/4			10–20	R8/2
		40–50	S3/5			20–30	R8/3
Fonyód	South	50–60	S3/6	Balaton-almádi	Middle	0–10	R9/1
		0–10	S4/1			10–20	R9/2
Zánka	North	10–20	S4/2			20–30	R9/3
		0–10	N3/1			30–40	R9/4
		10–20	N3/2	Balaton-kenese	Middle	0–10	R10/1
		20–30	N3/3			10–20	R10/2
		30–40	N3/4			20–30	R10/3
		40–50	N3/5			30–40	R10/4
		50–60	N3/6	Balatonvilágos	South	0–10	R11/1

Table 1(cont.)

Locality on shore	Position relative to long axis of lake	Depth from sediment surface (cm)	Sample identifier
Zánka	Middle	0–10	M3/1
		10–20	M3/2
		20–30	M3/3
		30–40	M3/4
		40–50	M3/5
		50–60	M3/6
Balaton-szemes	South	60–70	M3/7
		0–10	S5/1
		10–20	S5/2
		20–30	S5/3
		30–40	S5/4
Zamárdi	South	40–50	S5/5
		0–10	S6/1
		10–20	S6/2
		20–30	S6/3
		30–40	S6/4
Tihany	Middle	40–50	S6/5
		50–60	S6/6
		0–10	M4/1
		10–20	M4/2
Balatonfüred	North	20–30	M4/3
		30–40	M4/4
		40–50	M4/5
		0–10	N4/1
Balaton-almádi	North	10–20	N4/2
		20–30	N4/3
		30–40	N4/4
		40–50	N4/5
Balaton-kenese	Middle	0–10	N5/1
		10–20	N5/2
		20–30	N5/3
		30–40	N5/4
Balatonvilágos	South	40–50	N5/5
		50–60	N5/6
		0–10	M5/1
		10–20	M5/2
	Middle	20–30	M5/3
		30–40	M5/4
		40–50	M5/5
		0–10	S7/1
	South	10–20	S7/2
		20–30	S7/3
		30–40	S7/4

Locality on shore	Position relative to long axis of lake	Depth from sediment surface (cm)	Sample identifier
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Suspended particles collected in 2013:			
Fenékpuszt	Zala River	N/A	R0/F
Keszthely	Middle	N/A	R1/F
Szigliget	Middle	N/A	R2/F
Tihany	Middle	N/A	R6/F
Balatonkenese	Middle	N/A	R10/F

Sediment cores collected in 1992:			
Nyugati-övcasarna	South	0–10	To-19/1
		50–60	To-19/6
		100–110	To-19/11
Szigliget	Middle	110–120	To-30/12
		150–160	To-30/16
		200–210	To-30/21
		240–250	To-30/25
		290–300	To-30/30
		340–350	To-30/35
Fonyód	Middle	250–260	To-22/26
Zánka	North	50–60	To-33/6
		100–110	To-33/11
		250–260	To-33/26
		320–330	To-33/33
Siófok	South	0–10	To-27/1
		50–60	To-27/6
		100–110	To-27/11
		150–160	To-27/16
		250–260	To-27/26
		300–310	To-27/31
Balaton-almádi	North	340–350	To-27/35
Balaton-almádi	North	240–250	To-29/25

Table 2

Selected physical and chemical water parameters, measured in the Zala river and at five locations in Lake Balaton on April 17, 2013. (The concentrations of Mg, Ca, K, Na and S were determined using ICP-MS; HCO_3^- and Cl^- were determined by titration; n.d.: not determined)

Measured parameters	Zala River (R0)	Keszthely (R1)	Szigliget (R2)	Zánka (R3)	Tihany (R6)	Balatonkenese (R10)
T (°C)	16.7	14.3	12.6	11.9	12.5	10.8
pH	7.8	8.62	8.62	8.77	8.74	8.72
Conductivity (mS/cm)	569	725	796	805	829	833
Dissolved O_2 (mg/l)	7.8	10.64	11.7	11.87	10.9	11.13
Mg (mg/l)	15.9	44.5	57	63.5	68	70.5
Ca (mg/l)	69.8	63.3	53.7	40.8	34.6	31.7
K (mg/l)	3.53	5.36	6.68	7.44	8.15	8.36
Na (mg/l)	15.9	31.7	38.5	42.7	45.5	47
S (mg/l)	24.8	39.8	48.1	48	50.6	52.2
HCO_3^- (mg/l)	222.65	271.45	271.45	268.4	n.d.	268.4
Cl^- (mg/l)	16.43	32.37	37.85	n.d.	n.d.	55.28

at room temperature. Some physical and chemical parameters of the water were measured during sampling (such as temperature, electrical conductivity, pH, oxygen saturation), and the concentrations of dissolved species were determined using inductively coupled plasma mass spectrometry (ICP-MS) or titration (Table 2). We performed geochemical modeling using Geochemist's Workbench[®] standard version 9.0 (Aqueous Solutions LLC).

In addition to our sampling in 2013, we also used XRD data from two sets of samples that were collected in earlier studies. Hlavay and coworkers studied the concentrations and chemical speciation of metallic and organic pollutants in the sediment of the lake in a series of experiments (Hlavay and Polyák 2002; Szilágyi et al. 2002). In 2002, sediment cores 50 to 60 cm long were collected and processed in the same way as described above for the 2013 samples. While Hlavay and coworkers used XRD to study the basic mineralogical composition of the sediment (Polyák and Hlavay 2005), we used their 81 original diffractograms for the analysis of the relative abundances and structures of carbonate minerals (samples marked N, M and S in Table 1 and Fig. 1, in reference to north, middle and south, respectively).

Cserny and coworkers conducted studies of the sediments of Lake Balaton over a 20-year period, drilling 33 boreholes into the lake bed that reached the Pannonian basement (Cserny 1987; Cserny 1997; Cserny 2002). In this study we used and reinterpreted XRD data from 22 samples that were obtained from 6 different drillings that were performed in 1992 (Cserny 2002) (Fig. 1). Only two of the 22 samples were from the upper 50 cm of the sediment, and most came from

between 1 and 3 m sediment depth (samples marked 'T6' in Table 1). Particular samples were selected on the basis of the presence of Mg-calcite with a relatively high Mg content and the presumed appearance of protodolomite. Our goal was to use these samples to compare the features in the XRD patterns that result from the presence of protodolomite with the ones that were observed in the other series of samples collected from the upper half meter of the sediment. In this way we wished to identify structural features that result from diagenetic changes in the carbonates.

The samples from 2002 and 2013 were analyzed using the same procedures and the same X-ray powder diffractometer. After passing through a 63- μm sieve, the dry powder was ground in an agate mortar and mounted into a specimen holder by shaking. XRD patterns were obtained with a Philips PW1710 instrument, using CuK α radiation, a graphite monochromator, and a step size of 0.035°. The samples from the 1992 campaign were analyzed using the same type of diffractometer but with a step size of 0.04°.

Interpretation of XRD patterns

Sections of the XRD patterns in the 2θ range from 26° to 31.5°, including the 011 peak of quartz and the 104 peaks of calcite and dolomite, were used for the analysis of the relative abundances and the cell parameters of carbonate minerals (Fig. 2a). Within these sections of the patterns the experimental curves were simulated using a modeling software (CrystalDiffract®, CrystalMaker Software Ltd.). Instrumental parameters such as peak width and zero point were calibrated on the basis of the quartz 011 peak (Table 3). The majority of experimental XRD patterns could be simulated using two carbonate phases, Mg-calcite (defined here as calcite with a MgCO_3 content >2%) and dolomite (Fig. 2b). In some spectra the asymmetric shape of the Mg-calcite peak indicated the presence of at least two

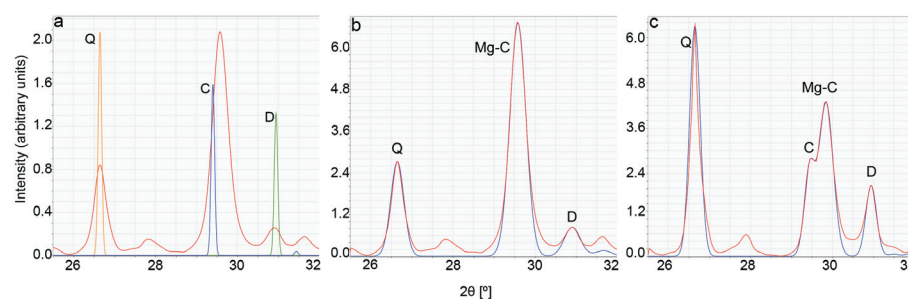


Fig. 2

Sections of X-ray powder diffractograms that were used for the analysis of calcite, Mg-calcite and dolomite cell parameters and relative concentrations. (a) An experimental curve with peaks calculated for stoichiometric quartz (Q), calcite (C) and dolomite (D). (b) and (c) Examples for the matching of experimental (red) and calculated (blue) profiles for quartz 011, Mg-calcite 104 (marked Mg-C) and dolomite 104 peaks. The Mg-calcite peak appears to be produced by a single phase in (b), whereas it splits into a calcite and a Mg-calcite peak in (c)

Table 3

Settings of the parameters that were used for simulating the 104 peaks of calcite, Mg-calcite and dolomite in XRD patterns

	Parameters	Calcite	Mg-calcite	Dolomite
Instrumental	Eta	constant (0.2)		
	Peak Width	constant (0.378 for the 2002 and 2013 samples, 0.306 for the 1992 samples, based on the quartz 011 peak)		
	Zero Correction	calibrated on the basis of the position of the quartz 011 peak		
Sample	Grain size	constant (>1000 nm)	varied, based on simulation of the 104 peak profile	varied, based on simulation of the 104 peak profile
	Unit cell	constant ($a_0 = 4.99 \text{ \AA}$, $c_0 = 17.059 \text{ \AA}$)	a_0 and c_0 varied, based on the position of the 104 peak (see Fig. 3a)	a_0 and c_0 varied, based on the position of the 104 peak (see Fig. 3b)

different calcite-type structures. In these cases we assumed the presence of stoichiometric calcite (defined here as calcite with a MgCO_3 content <2%) in addition to Mg-calcite, and modeled the XRD pattern using three carbonate phases: calcite, Mg-calcite and dolomite (Fig. 2c). For modeling the calcite 104 peak, neither the cell parameters, nor the grain size were adjusted. The positions and shapes of the peaks from both Mg-calcite and dolomite were fitted manually by adjusting the cell parameters and varying the average particle size, respectively (Table 3). Since the a_0 and c_0 cell parameters are not independent of each other, they were co-adjusted, as described below.

The observed changes in the cell parameters of calcite and dolomite have long been interpreted as resulting from deviations from the ideal compositions in both phases (Goldsmith and Graf 1958). The incorporation of the smaller Mg^{2+} cation into the Ca^{2+} site causes a contraction of the unit cell of calcite, whereas a

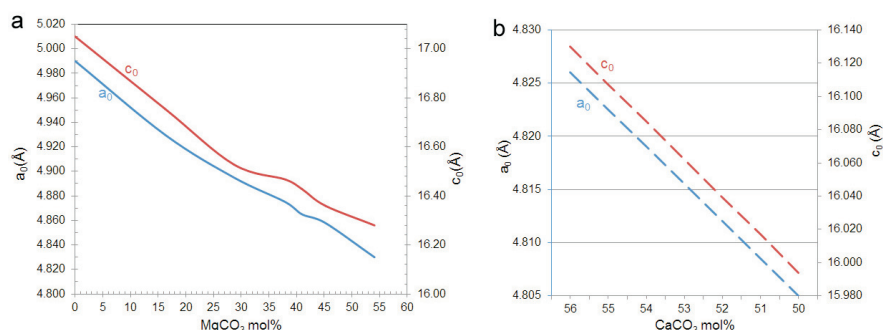


Fig. 3

Variation of the a_0 and c_0 cell parameters (a) with Mg-content in Mg-calcite having a disordered distribution of cations, based on Zhang et al. (2010), and (b) with Ca-content in dolomite, based on Turpin et al. (2012)

higher-than-stoichiometric Ca/Mg ratio in dolomite results in the expansion of its unit cell. The relationship between the changes in the Mg/Ca ratio and the variation of the cell parameters is almost linear for disordered structures with a MgCO_3 content between 0 and 30% (Reeder and Sheppard 1984; Zhang et al. 2010). Thus, for modeling the Mg-calcite 104 peak we derived the relationship between a_0 and c_0 from the empirical curve obtained by Zhang et al. (2010) (Fig. 3a), and simply converted the observed 104 d-spacings into compositions.

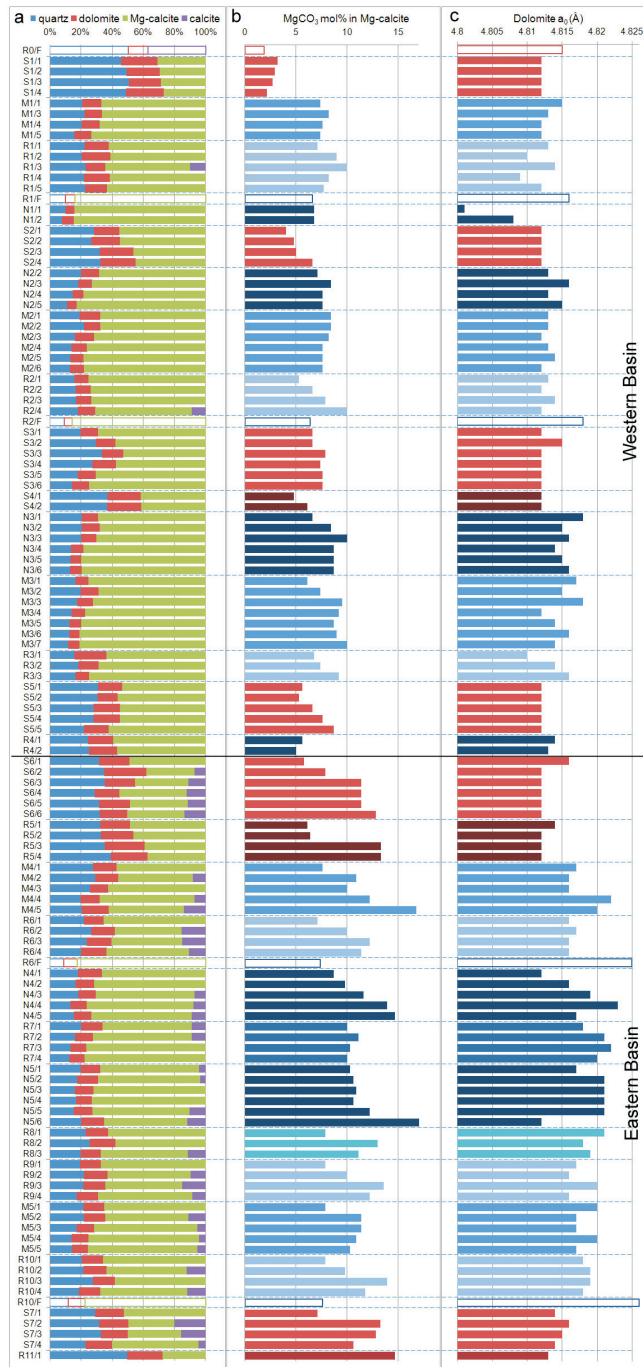
The variation of the cell parameters of phases with compositions close to that of dolomite (between 30 and 50% MgCO_3) is more complex. Synthetic Mg-calcites with completely disordered arrangements of Ca and Mg ions have significantly larger cell parameters than dolomite (Zhang et al. 2010) (Fig. 3a). However, various partially ordered arrangements of Mg and Ca are known for intermediate compositions between calcite and dolomite that may result in non-linear changes of structural parameters (Wenk et al. 1983; Reeder 1992; Ruiz-Agudo and Rodriguez-Navarro 2013). One of these phases might be “protodolomite”, which produces a distinct peak near $2\theta = 30.5^\circ$ in XRD patterns. In the case of the samples discussed in this study, however, we did not observe local ordering using transmission electron microscopy (results are not shown here), and protodolomite peaks were observed in a few cases only. In most samples the observed dolomite cell parameters were close to those of ordered, stoichiometric dolomite. Slight variations in the parameters of natural, low-Fe dolomite (Eocene and older) were observed in several earlier studies and generally attributed to deviations from the ideal Ca/Mg ratio (Reeder and Sheppard 1984; Turpin et al. 2012). While some studies found that the a_0 and c_0 parameters showed good correlation with the CaCO_3 excess only in the range above 52.5 mol% (Reeder and Sheppard 1984), an empirical study resulted in a linear model between cell parameters and Ca excess even closer to the ideal dolomite composition (Turpin et al. 2012). In order to model the dolomite peaks in our XRD spectra, we co-varied the a_0 and c_0 parameters by using the lines given by Turpin et al. (2012) (Fig. 3b).

Results

The elongated shape and the geographic orientation of Lake Balaton have important influences on sediment formation. Therefore, the results of our XRD analyses are presented and discussed below in relation to the variations in lake water chemistry and sediment physical properties along the W-E and N-S directions, respectively.

The mineralogical compositions, the Mg content of Mg-calcite, and the a_0 parameter of dolomite are shown in Fig. 4 for the two sets of sediment samples from 2002 and 2013 that were collected using the same procedure. Several sampling locations were identical in these two campaigns (Fig. 1), offering an opportunity to observe changes in sediment properties over the last ten years. However, XRD patterns from the pairs of samples which were collected 11 years apart (such as

Fig. 4
Results of the analysis of X-ray powder diffractograms of series of sediment samples and five suspended particulate matter samples collected in 2002 and 2013 from Lake Balaton, arranged according to geographic location, from west (top) to east (bottom), and according to sample depth relative to the sediment surface. Dashed horizontal lines separate sample series from different sediment cores. (a) Relative mass concentrations of quartz, Mg-calcite, dolomite and calcite. The color code is given at the top of the panel. (b) MgCO_3 content of Mg-calcite, and (c) the a_0 cell parameter of dolomite, derived from the measured positions of the Mg-calcite and dolomite 104 peaks, respectively. In (b) and (c) columns in shades of brown represent samples from near the south shore, whereas columns in shades of blue represent samples from the middle of the lake and from near the north shore. Empty columns stand for suspended matter samples



M1–R1, M2–R2, M3–R4, M4–R6, M5–R10 and S7–R11) were essentially indistinguishable, so the results from the two campaigns are shown combined in Fig. 4. In addition, we also show the results from the five samples that contained suspended particles filtered from the water.

Mineralogical composition and grain size

From the XRD patterns we determined the relative ratios of quartz and the three carbonate minerals (calcite, Mg-calcite and dolomite) (Fig. 4a). Sheet silicates (mica and clay minerals) and feldspars (mainly albite) were also present in the samples but we did not determine their concentrations because they typically occurred in minor amounts (with their combined fraction <20%), and their relative abundances correlated with that of quartz. Therefore, a rough estimate of the amount of the detrital mineral fraction in the sediment can be made on the basis of the amount of quartz. As expected, the relative quartz contents of the samples from near the south shore are typically larger than from the north **one** and the middle of the lake (Fig. 5). No systematic changes in the sediment mineralogical composition are apparent, either along the W–E axis of the lake, or with specimen depth within each individual sediment core (Fig. 4a). The ratios of quartz, dolomite and Mg-calcite are remarkably constant in the four samples of suspended particles that were obtained from the lake water.

The major phase in almost all samples is Mg-calcite, with its concentration varying from 27 to 85%. Dolomite is a minor phase in all samples, with concentrations between 5 and 27%. The data points in Fig. 5 appear to scatter about a line that connects the Mg-calcite corner with the quartz-dolomite tie line, suggesting a nearly constant ratio and, consequently, a similar origin of quartz and most of the dolomite. Suspended particles in the Zala River and sediment samples from Fenékpuszta which essentially represent the alluvial fan of the Zala (S1 samples; see Table 1 and Fig. 1), are richer in quartz than all other samples and produce data points off the trendline in Fig. 5. The four samples of suspended particles that

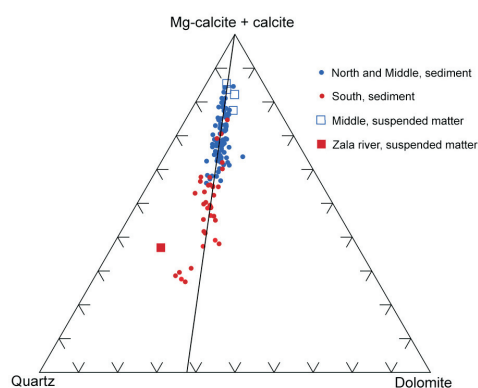


Fig. 5

Graphic representation of the geographic distribution (south vs. north and middle) of the relative ratios of quartz, dolomite and Mg-calcite+calcite in the samples shown in Fig. 4, as derived from XRD patterns. The compositions of five suspended matter samples (one from the Zala River and four from the lake) are also shown

were obtained from the lake water are among the samples that contain the largest fraction of Mg-calcite (>80%).

The changes in mineralogical compositions along the N–S axis are related to variations in typical grain sizes. Owing to the prevailing northerly winds, coarser, sand-sized sediment grain fractions accumulate in a shallow bank that stretches along the south shore, whereas along the center and the north shore of the lake most of the sediment consists of silt-sized particles. The presence of coherently diffracting domains smaller than ~100 nm cause peak broadening in the XRD patterns. Such peak broadening was not observed for quartz in any of our samples, indicating relatively large grain sizes, consistent with its detrital origin. On the other hand, Mg-calcite invariably displayed a broad peak that could be modeled with grain sizes ranging from 21 to 44 nm. Since dolomite was a minor component in all samples and typically produced a low-intensity peak, its grain size could be modeled less precisely than that of Mg-calcite. Nevertheless, while samples from the Western Basin contained dolomite with >100-nm grain size, in some samples from the Eastern Basin the dolomite peak was broad and could be modeled with grain sizes from 26 to 44 nm.

The grain sizes derived from XRD patterns were compared with data obtained using microscopy techniques including scanning and transmission electron microscopy, as well as atomic force microscopy (results not shown here). Microscope images confirm the large (from several to tens of μm) sizes of quartz grains, whereas Mg-calcite typically forms 2 to 5 μm -sized aggregates that consist of smaller crystallites. The XRD-derived grain sizes probably correspond to the sizes of individual crystallites within these aggregates. Dolomite grains in filtered samples from the Eastern Basin were identified in electron microscope images as <2 μm -sized single crystals. Thus, a reconciliation of grain size data obtained from XRD and microscopy techniques will require further study.

Mg-calcite

Our results confirm several earlier conclusions (Müller and Wagner 1978; Cserny 2002; Tullner 2002; Tullner and Cserny 2003) but also provide new information on carbonate formation in Lake Balaton. Although the Mg content of Mg-calcite was reported in these previous studies, there is no detailed information on the applied technique of its analysis. Since we used the same procedure for interpreting XRD patterns from four sets of samples, our data are internally consistent and allow us to compare spatial and temporal changes (i.e., with geographic location and with sediment depth, respectively) in the cell parameters and, consequently, in the Mg content of Mg-calcite.

Within the upper half meter of the sediment, the MgCO_3 mol% of Mg-calcite varies between 2 to 17% (Fig. 4b). The most striking feature of the distribution of Mg-calcite compositions is an increase of the Mg content from west to east, with an abrupt change between the Western and Eastern Basins of the lake. Suspended

Mg-calcite particles show a slight increase in their MgCO_3 content from west to east, from 6.6% near Keszthely (R1/F) to 7.6% at Balatonkenese (R10/F).

Concerning the variation of the Mg content with depth, there is no universal pattern in every sample series; however, in many samples, particularly in the Eastern Basin, the Mg content of Mg-calcite increases down-section (Fig. 4b). In the XRD patterns of samples in which the MgCO_3 mol% in Mg-calcite exceeds 12%, the 104 calcite peak splits into a calcite (with 1 to 2% MgCO_3 content) and a Mg-calcite peak (Fig. 2c). For such samples only the Mg-content of the high-Mg-calcite is shown in Fig. 4b. Thus, the maximum MgCO_3 concentration of Mg-calcite as a single phase, the XRD peak of which can be faithfully reproduced in our modeling experiments is 17% (in all three sets of sediment samples). In some samples there is a hump-like feature in the XRD pattern between the peaks of calcite and dolomite that cannot be modeled using a single Mg-calcite phase. We assume that in these samples a range of compositions occurs, as is discussed below in the section on protodolomite.

Dolomite

Since dolomite is a minor component in our samples, it produces a relatively low-intensity 104 peak in the XRD patterns (Fig. 2). Nevertheless, a shift in the position of this peak between different samples is clearly observable. The observed variation of the dolomite cell parameters appears to follow a distinct pattern (Fig. 4c), with larger values occurring in the samples from the Eastern Basin.

Small variations in the cell parameters of dolomites may not necessarily reflect compositional anomalies. The structure of ordered, stoichiometric dolomite was determined in several studies, and a range of cell parameters were given. For example, the a_0 parameter was found to be as small as 4.804 Å (Reeder and Wenk 1983), and as large as 4.812 Å (Effenberger et al. 1981). Nevertheless, the analyses of cell parameters and compositions of a large number of sedimentary dolomite samples indicated that a_0 parameters larger than 4.812 Å are indeed associated with Ca excess, approximately following the relationship illustrated in Fig. 3b (Reeder and Sheppard 1984; Turpin et al. 2012). Therefore, in our samples we consider the observed dolomite cell parameters anomalous only if a_0 exceeds 4.812 Å.

The dolomite a_0 value is smaller than 4.812 Å in only five of our samples, all of which come from the Western Basin, four from the westernmost part of the lake, near Keszthely (R1/2, R1/4) and Gyenesdiás (N1/1, N1/2). Many samples from the Western Basin and from the south shore contain dolomite with $a_0 = 4.812$ Å. On the other hand, dolomite has anomalously large cell parameters in many samples from the Eastern Basin (Fig. 4c), suggesting that its MgCO_3 content is less than 50%. Clearly the anomalous dolomite values are characteristic for the same samples in which the Mg-calcite has a high (>10%) MgCO_3 content, that is, mostly in the Eastern Basin, in the samples from the north shore and the center of

the lake. In contrast to the Mg content of Mg-calcite, the anomalous composition of dolomite does not change according to a clear pattern with sediment depth; instead, its variation appears to be quite random. Another remarkable feature of the distribution of dolomite a_0 parameters is a steady increase from west to east in the samples of suspended particulate matter. In fact, the deviation from ideal values is significantly larger in the suspended dolomite particles than in the sediment samples at the same locations. The largest value (4.826 Å) was observed in suspended matter filtered near the eastern end of the lake, at Balatonkenese (R10/F, Fig. 4c), corresponding to a CaCO_3 content of ~56 mol% (Fig. 3b).

Protodolomite

As mentioned in the Introduction, “protodolomite” is a widely but inconsistently used term in the literature for phases that have dolomite-like compositions and a partially ordered distribution of Ca and Mg in their structures (Gaines 1977). In order to be consistent with earlier studies of Lake Balaton sediments (Müller 1970; Cserny et al. 1991), in this paper we restrict the term “protodolomite” to a phase that produces a distinct peak in the XRD pattern at $2\theta \sim 30.5^\circ$. In the XRD patterns of some of the selected samples from the 1992 sample set (To-33/6, To-33/11, To-33/33, To-27/26, and To-29/25) an extremely broad carbonate 104 peak appears that cannot be modeled by using three carbonate phases (calcite, Mg-calcite, dolomite) (Fig. 6). In some spectra, within this broad peak a small maximum occurs at $2\theta \sim 30.5^\circ$, probably reflecting the onset of ordering of Mg and Ca ions in the structure. A similar peak occurs in several specimens from the other two sets of sediment samples (Fig. 7), indicating the presence of minor protodolomite. In contrast, protodolomite does not occur in any of the suspended particulate samples.

It needs to be emphasized that the anomalous cell parameters of dolomite are not associated with protodolomite formation. The observed position of the dolomite 104 peak ranges from $2\theta = 31.0^\circ$ to 30.8° (corresponding to a cell with $a_0 = 4.826$ Å in sample R10/F), whereas the protodolomite peak appears at $2\theta = 30.5^\circ$. Based on the distinct peak it produces in the XRD pattern and its different pattern of distribution in the sediment, we conclude that protodolomite is distinct from dolomite and forms by different processes.

It is noteworthy that even though the 1992 samples analyzed in this study were obtained from deeper layers of the sediment than the 2002 and 2013 samples, both the Mg-content of Mg-calcite and the cell parameters of dolomite show similar values in the three sets of samples, at least in those samples in which the peaks belonging to these phases could be modeled. In the 1992 sample set the MgCO_3 content of Mg-calcite does not exceed 16 mol% (Fig. 6b), and the dolomite a_0 parameter varies from 4.812 to 4.823 Å, with larger values occurring in the samples from the north shore and the Eastern Basin (Fig. 6c).

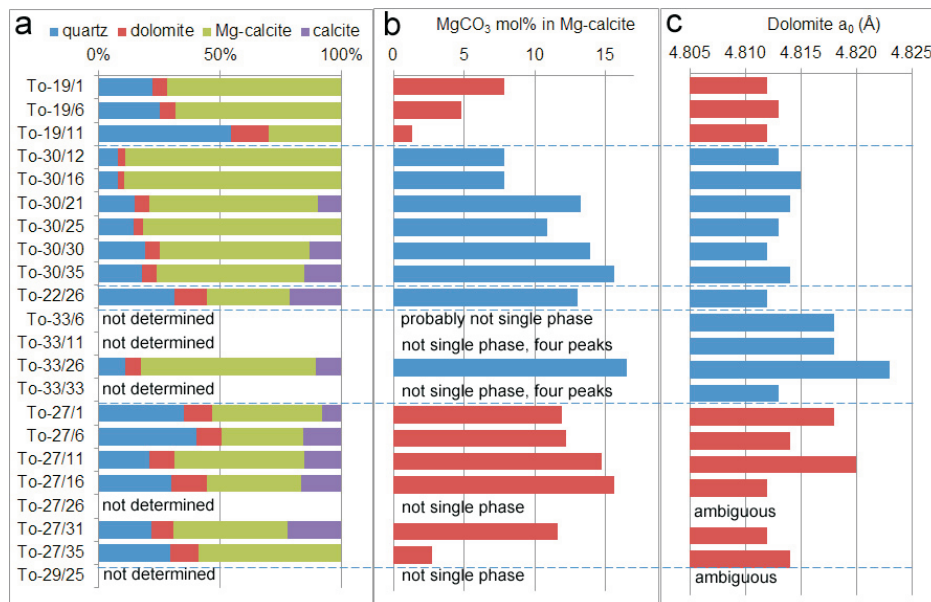


Fig. 6

Results of the analysis of X-ray powder diffractograms of series of samples from cores cut in 1992, arranged according to geographic location, from west (top) to east (bottom), and according to sample depth relative to the sediment surface. Dashed horizontal lines separate sample series from different sediment cores. (a) Relative mass concentrations of quartz, Mg-calcite, dolomite and calcite. (b) MgCO_3 content of Mg-calcite, derived from the measured position of the 104 peak. (c) The a_0 cell parameter of dolomite, derived from the measured position of the dolomite 104 peak. In (b) and (c) columns in shades of brown represent samples from near the south shore, whereas columns in shades of blue represent samples from the middle of the lake and from near the north shore

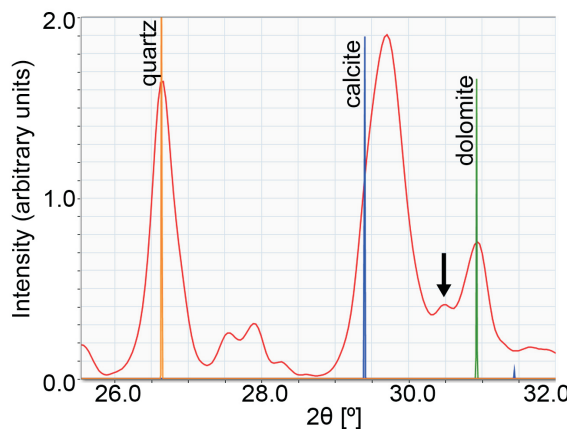


Fig. 7

A section of an X-ray powder diffractogram obtained from a sediment sample from Balatonvilágos (S7/4), showing a distinct peak of protodolomite at $2\theta = 30.5^\circ$ (arrowed)

Discussion

The major goal of this study was to understand the mineralogical character of particles that directly precipitate from the water. Since the April 17, 2013 samples were collected under very calm conditions, we assume that among all samples discussed in this study the filtered samples of suspended material are the most representative of such particles (R1/F, R2/F, R6/F, and R10/F). On the other hand, the sample filtered from the water of the Zala River (R0/F) gives some clues about the composition of the detrital input.

An obvious relationship exists between the water chemistry (especially the Mg/Ca ratio) and the composition of suspended Mg-calcite particles. At the time of the 2013 sampling a strong W–E chemical gradient was present in the lake, as a result of flooding of the tributaries, including the Zala River. The electrical conductivity ranged from 725 (Keszthely, R1) to 833 mS/cm (Balatonkenese, R10), as a result of the increasing concentrations of electrolytes (Na^+ , K^+ , Mg^{2+}) toward the eastern end of the lake (Table 2). A strong gradient of the Mg/Ca mass concentration ratio occurred, changing from 0.70 (Keszthely, R1) to 2.22 (Balatonkenese, R10). Whereas the calcite carried by the Zala River contained only 2 mol% MgCO_3 , in the four samples of suspended matter filtered from the lake the MgCO_3 content varied between 6.4 and 7.6%, and increased slightly from W to E (Fig. 4b). We consider these values as representative of the composition of Mg-calcite that directly precipitated from the water under the particular conditions of the sampling.

Concerning the dolomite fraction of the suspended matter, a surprising, linear relationship is apparent between the Mg/Ca ratio in the water and the cell parameters of dolomite. In former studies the dolomite fraction in the sediments of Lake Balaton was considered to result exclusively from the erosion of Triassic rocks that are exposed in large areas north of the lake (Müller and Wagner 1978). While such detrital dolomite is certainly present in the lake sediments, the observed pattern of cell parameter changes suggests that the origins of dolomite might be more complex than previously thought.

We interpret our results as providing weak, indirect evidence that dolomite precipitates directly from the lake water. The parallel pattern of lake water chemistry and increasing cell parameters of dolomite (and, consequently, its non-stoichiometric, Mg-deficient composition) from west to east (Fig. 4c) suggest that the anomalous dolomite cell parameters are related to the chemical gradients in the lake water. Although many genetic and morphological types of Triassic dolomites are present in the catchment area (Haas et al. 2012; Haas et al. 2014), it is unrealistic to assume that a distinct compositional gradient in dolomite occurs from west to east among the outcrops that are the origins of the detrital grains carried by the streams and wind into the lake. The small grain size of dolomite in the suspended matter (in the micrometer range, according to electron microscopy results that are not shown here) also supports the possibility of direct precipitation. Along the

south shore, where the mud is rich in quartz and characterized by larger grain sizes, no distinctive changes of dolomite cell parameters can be observed, suggesting that in these samples most of the dolomite grains have compositions close to stoichiometric and are of detrital origin. Thus, we tentatively assume that the dolomite peaks measured in our XRD patterns are actually composites produced by mixtures of detrital and freshly precipitated dolomite grains. While the structures of the two phases do not deviate significantly enough to produce an observable split of the 104 peak, the position of this peak is influenced by the relative amount of structurally more anomalous, presumably primary, dolomite in the mixture.

Interestingly, according to our thermodynamic modeling calculations, ordered dolomite should be the stable carbonate phase that precipitates from the water at conditions that are typical for Lake Balaton (Fig. 8). On the other hand, it is well known that at room temperature and atmospheric pressure the nucleation of dolomite is kinetically hindered (Sibley et al. 1994; Land 1998). In most systems where contemporary dolomite formation is observed, the process is microbially mediated (Machel 2004). In the case of the anomalous dolomite in Lake Balaton, the potential roles of microorganisms in its formation certainly cannot be excluded; however, at the moment we have no evidence for such microbial processes and all further discussion of microbially-assisted dolomite formation would be pure speculation.

Concerning the 104 peak of Mg-calcite, in most cases it is also produced by at least two phases: detrital calcite and primary Mg-calcite. However, in contrast to dolomite, the primary material (Mg-calcite) is the dominant phase, particularly in samples from the middle of the lake and from the vicinity of the north shore (Fig. 5). Thus, in these samples the variations of the cell parameters of Mg-calcite can be safely assumed to reflect autochthonous processes.

The cell parameters of Mg-calcite in the sediment show similar trends as in the suspended particles. However, at each sampling location the Mg content of

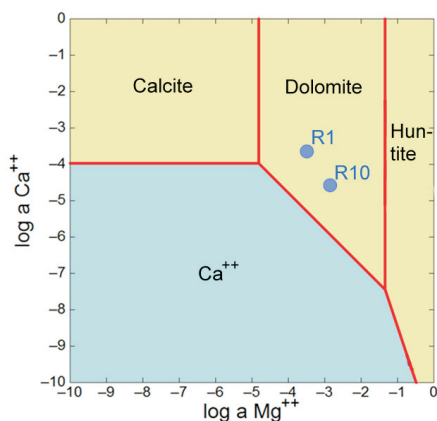


Fig. 8

The result of geochemical modeling (at $T = 13\text{ }^{\circ}\text{C}$ and $\text{pH} = 8.3$) of carbonate precipitation as a function of Mg^{2+} and Ca^{2+} activities indicates that dolomite is the thermodynamically stable solid phase at conditions that are typical for the water of Lake Balaton. The data points R1 and R10 were calculated using Mg and Ca concentrations measured at Keszthely (R1) and Balatonkenese (R10) on April 17, 2013 (see Table 2)

Mg-calcite is typically larger in the sediment than in the suspended matter (Fig. 4b). In addition, in many cases the Mg content increases with sediment depth. These features can be explained by diagenetic changes, a progressive Mg enrichment through the equilibration of the deposited Mg-calcite grains with Mg-rich pore water, as suggested earlier (Müller and Wagner 1978). As the Mg content increases and reaches about 17%, continuous intensity appears between the Mg-calcite and dolomite 104 peaks, in some cases decorated by small additional peaks, among which the most distinct is that of protodolomite (Fig. 7). Thus, the 104 Mg-calcite peak can be modeled as produced by a single phase only up to ~17% MgCO_3 content. Beyond this composition ($\text{Ca}_{0.83}\text{Mg}_{0.17}\text{CO}_3$) an almost continuous range of Mg content exists, probably with structures having mostly disordered Mg/Ca distributions, punctuated by certain ordered arrangements, such as the one producing protodolomite. Since no distinct maximum occurs between the 104 peaks of protodolomite and (anomalous) dolomite (from ~ 30.5 to $30.8^\circ 2\theta$), our data suggest that diagenetic dolomitization in the sediments of Lake Balaton progresses from Mg-calcite only as far as protodolomite. As a summary of our observations, a scheme of the precipitation and diagenetic changes of carbonate minerals is shown in Fig. 9.

What is the implication of these observations concerning the effects of climatic changes and weather extremes on sediment formation? The degree of super-

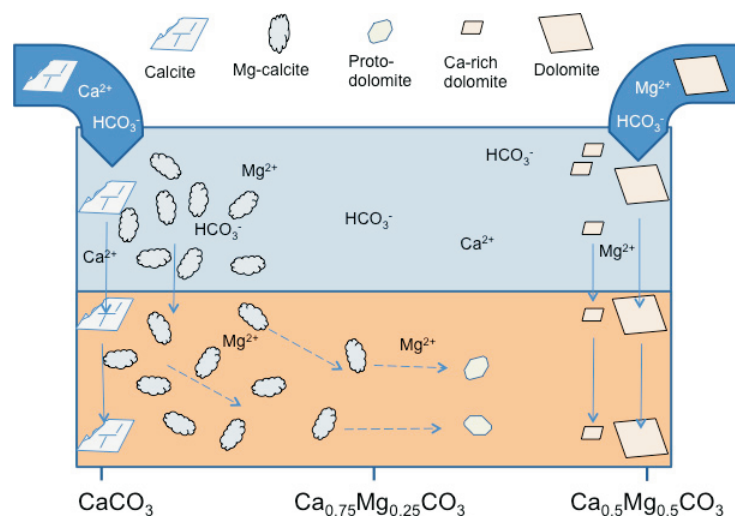


Fig. 9

Schematic diagram illustrating the fate of carbonate minerals in Lake Balaton, set in the compositional space between calcite (CaCO_3) and dolomite ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$). The upper, blue part represents water and the lower, brown part the sediment. Detrital calcite, dolomite and dissolved species are delivered by the Zala River and other inflows. Mg-calcite and anomalous, Ca-rich dolomite precipitate within the lake, and Mg-calcite transforms into protodolomite within the sediment. Solid arrows indicate deposition of particles, whereas dashed arrows show the aging process in the sediment

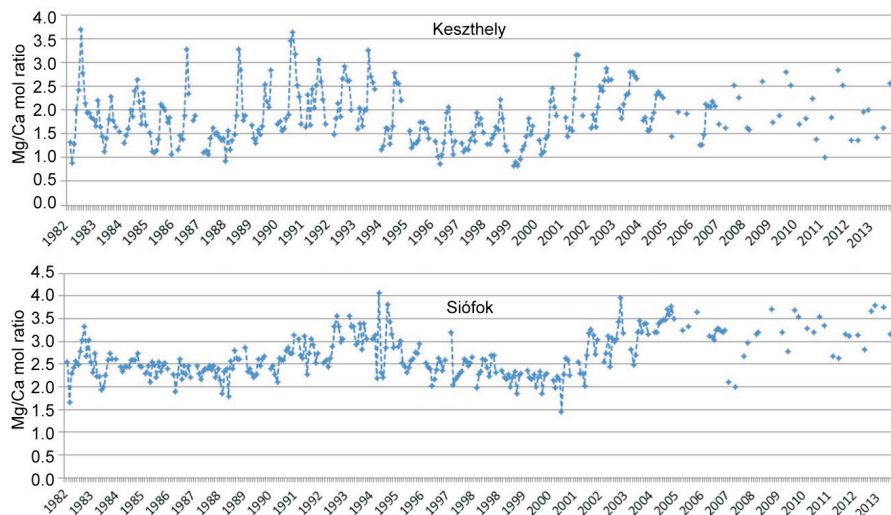


Fig. 10
Variation of the mol ratio of dissolved Mg and Ca from 1982 to 2013, measured at Keszthely (Western Basin) and Siófok (Eastern Basin) by the Central Transdanubia Environmental Protection and Conservation Directorate

saturation of the lake water with respect to carbonate minerals depends on temperature, pH and water chemistry. Among these factors, the changes in the Mg/Ca ratio are most important in governing which carbonate phase is thermodynamically stable (Fig. 8). Annual and seasonal variations in the Mg/Ca ratio of the lake water are illustrated by a 30-year data series measured by the Central Transdanubia Environmental Protection and Conservation Directorate at two locations, Keszthely (Western Basin) and Siófok (Eastern Basin) (Fig. 10). Seasonal variation is more pronounced at Keszthely, which is situated close to the inflow of the Zala River, than at Siófok. The average Mg/Ca ratio is significantly higher at Siófok than at Keszthely. Variations on a decadal timescale are also observable: the last ten years are characterized by higher Mg/Ca ratios than in the preceding period (unfortunately, the measurements were done on an irregular basis after 2004, as seen from the graphs), due to the occurrence of several extreme minima in the water budget. Such variations in lake water chemistry should indeed affect the relative ratios of the distinct, precipitating carbonate phases and their Mg contents, and thus influence the mineralogical character of the sediment. Simply put, dry periods result in a high Mg/Ca ratio in the water that triggers the formation of Mg-calcite with a higher Mg content than do wet periods, consistent with the results of earlier studies (Müller and Wagner 1978; Tullner 2002; Tullner and Cserny 2003). If our assumptions about the precipitation of anomalous dolomite are correct, then the chance for the formation of primary dolomite is also higher during dry periods when the lake water is less diluted and contains more dissolved Mg than during wet periods.

Unfortunately, the physical characteristics of Lake Balaton do not permit a reconstruction of climatic events with a decadal time resolution. The turbulence in the shallow lake thoroughly mixes the upper 3 to 5 cm of the mud. Waves and currents move and redeposit sediment material, resulting in strong variations in the sediment accumulation rate by location, as was shown by studies of sediment isotopic compositions (Cserny et al. 1995). As a result, typically there are no distinct layers in the mud from which the extreme periods could be traced using the Mg content on a decadal basis. In addition, since on average between 5 to 50 cm of sediment accumulated in the last 100 years, depending on location (Cserny and Nagy-Bodor 2000; Korponai et al. 2011), it cannot be expected that a marked change in sediment composition could be observed as a result of weather extremes within the last ten years. For a decadal or even annual or seasonal time resolution, other techniques such as the analysis of bivalve shell isotopic compositions can be used (Schöll-Barna 2011; Schöll-Barna et al. 2012). However, over longer time scales, even though diagenetic processes may mask some of the effect, climatic changes can be identified on the basis of the Mg content of Mg-calcite, as was shown in earlier studies (Müller and Wagner 1978; Tullner and Cserny 2003). In conclusion, although the increasing frequency of weather extremes of the last ten years should affect the composition of depositing minerals, for reasons detailed above this effect is not strong enough to result in a detectable change in the mineralogical characteristics of the upper layers of Lake Balaton sediments.

Concluding thoughts

We demonstrated the presence of four different carbonate minerals in Lake Balaton: calcite (with a MgCO_3 content < 2 mol %), Mg-calcite (2 to 17 mol% MgCO_3), protodolomite and dolomite. According to thermodynamic considerations, the lake water is supersaturated with respect to both calcite and dolomite (calcite should precipitate even from the Zala River). The degree of supersaturation is controlled, at least partly, by the amount of water supply, resulting in a W–E gradient in both lake water chemistry and suspended and sediment mineral compositions. An increasing Mg/Ca ratio toward the eastern part of the lake results in higher Mg contents in the precipitating Mg-calcite.

Concerning the presence of dolomite in Lake Balaton sediments, for the first time we analyzed and reported variations in its cell parameters. The similar pattern of spatial distribution of dolomite and Mg-calcite anomalies are intriguing and suggest that at least a small fraction of the dolomite present in the sediment likely is of a primary origin. The potential precipitation of dolomite from the lake water deserves further study. However, for obtaining unambiguous data on the origins of this minor phase, it needs to be separated from the rest of the sediment, which poses a major challenge, given the occurrence of at least four different but similarly behaving carbonate minerals in the system. Nevertheless, experiments

aiming at the separation of dolomite are under progress and, pending their success, analyses of trace element and stable isotopic compositions are planned.

The results of our present study highlight several other, potentially interesting scientific problems. These include the roles of algae both in controlling water chemistry through photosynthesis and in potentially providing surfaces for Mg-calcite nucleation (Dittrich and Obst 2004), as well as the relationships between the compositions and crystallographic features of the precipitating Mg-calcite. Another outstanding problem is the reworking and packaging of carbonate minerals by filtering organisms including zooplankton and mussels (G.-Tóth and Zánkai 1985), resulting in significant changes in the grain sizes of the primary minerals. These problems are being addressed mainly by individual particle studies using electron microscopy techniques, and will be reported on in the future.

Acknowledgements

We dedicate this study to the memory of Professor József Hlavay who performed extensive research on the nature of pollution in Lake Balaton, and whose XRD data are used in this work. We thank László Merényi for performing the XRD analyses, and Géza Dobos for his help with the 2013 sample collection. We acknowledge Tamás Fancsik for granting us permission to use the data collected by the predecessor of the Hungarian Geological and Geophysical Institute in 1992. Water chemistry data were kindly provided by Gábor Kiss from the Central Transdanubia Environmental Protection and Conservation Directorate, Siófok, Hungary. This study was supported by the European Union with co-funding by the European Social Fund, under project number TÁMOP-4.2.2.A-11/1/KONV-2012-0064.

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