

Transmission Electron Microscopy Highlighted the Importance of Clay Minerals in the Dolomitization of Ca-Mg Carbonates in a Hypersaline Soda Lake

Olga S. Burakova^{1,2}, Lyubov V. Zaytseva², Maria A. Sinetova³, Alexandra G. Markelova³

¹ Winogradsky Institute of Microbiology, Federal Research Centre “Fundamentals of Biotechnology”, Russian Academy of Sciences, Moscow, Russia

² Borissiak Paleontological Institute, Russian Academy of Sciences, Moscow, Russia

³ Timiryazev Institute of Plant Physiology, Russian Academy of Sciences, Moscow, Russia

INTRODUCTION & AIM

Hypersaline Petukhovskoe Soda Lake (Southwestern Siberia, Russia) is characterized by the development of huge biomass of phototrophic communities, which accumulates near the shoreline and gradually dries out, finally forming cavernous crusts that later become stromatolites with stoichiometric dolomite in their composition. Exopolysaccharides (EPS) have previously been shown to play a crucial role in their formation (Samylina, Zaytseva, 2018).

This work aimed to study the specifics of Ca-Mg carbonate formation in this lake via transmission electron microscopy.

MATERIALS & METHODS

Three samples (S1, S2, and S3) were collected simultaneously in the littoral at different distances from the water and represent successive stages (from S1 to S3) of phototrophic biomass desiccation.

- The mineral composition of the samples was studied using Fourier Transform Infrared Spectrometer FT/IR-4100 (Jasco, Japan).
- The study of samples using transmission electron microscopy with energy-dispersive X-ray spectroscopic analysis (TEM-EDX) was carried out on a JEM 1400 electron microscope (JEOL, Japan) equipped with an INCA Energy TEM 350 X-ray microanalysis system (Oxford Instruments, UK).

RESULTS & DISCUSSION

TEM-EDX allows for visual differentiation of structural components in all samples (figs. 1, 2):

- [1] free clay particles,
- [2] fine clay particles surrounding cell walls,
- [3] a completely interstitial clay-EPS matrix, and
- [4] Ca-Mg carbonate crystals of varying sizes embedded in this matrix.

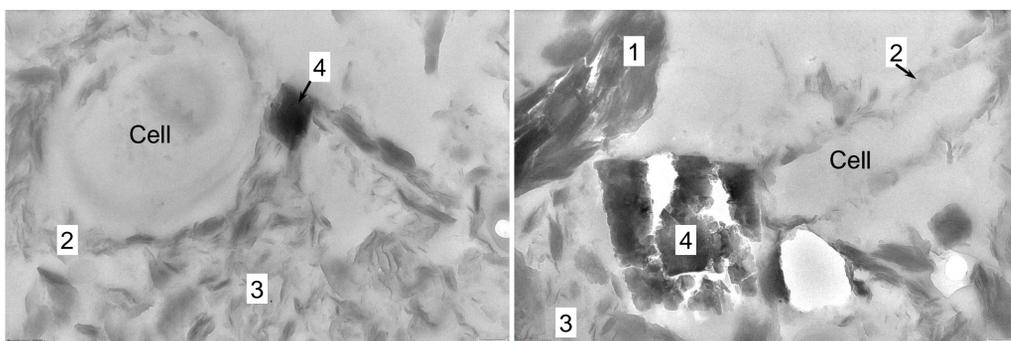


Figure 1. Structural components of the studied samples. Magnification $\times 50000$, scale 200 nm.

- The elemental composition of the clay components corresponds to montmorillonite $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (figs. 2).
- The Mg/Ca ratio in carbonate crystals varies from low-Mg calcite to dolomite (table 1).

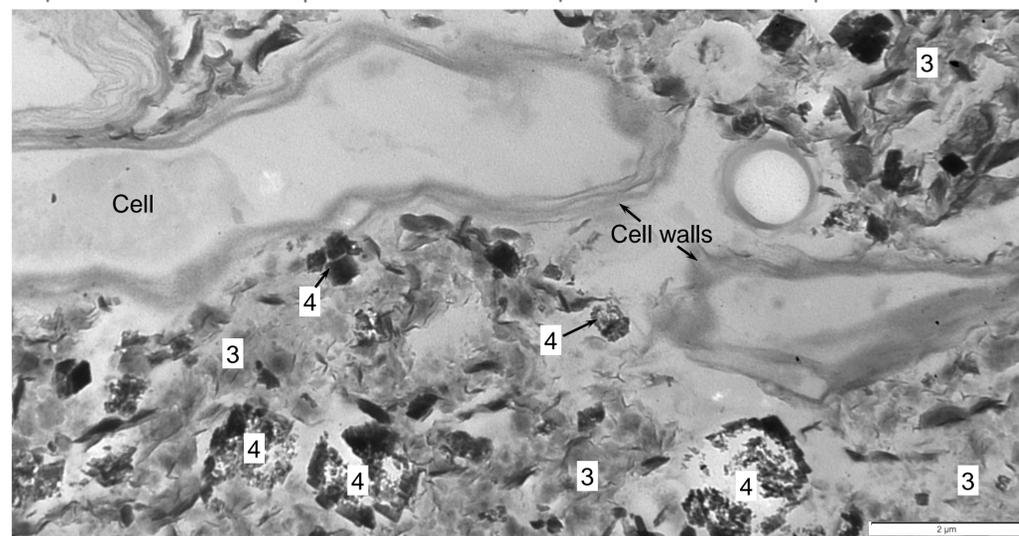
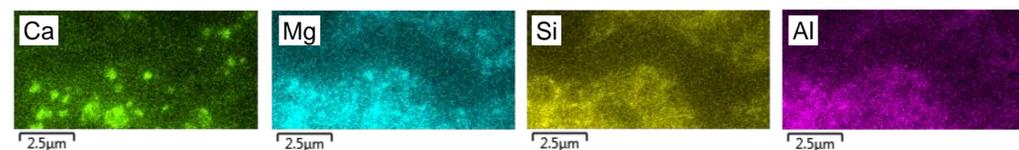


Figure 2. TEM-EDX of a section of sample S3 showing the composition of all components. Magnification $\times 20000$, scale 2 μm .

Table 1. Maxima of the characteristic bands in the IR spectra of the studied samples in the absorption region of Ca-Mg carbonates.

Sample		Position of characteristic bands, cm^{-1}			Ca-Mg carbonates
		ν_2	ν_3	ν_4	
S1	a,b,c	879	1423	727, 726, 725	High-Mg calcites
	d	878	1436	729	Dolomite
S2	a	879	1430	729	Dolomite
	b	879	1430, 1428	728, 717	Ca-excess dolomite, low-Mg calcite
	c	878	1430	729, 716	Dolomite, low-Mg calcite
S3	a,b,c,d	879, 878	1435, 1434	729, 728	Dolomite
	e	879	1434	729, 719	Dolomite, low-Mg calcite

A transition from predominantly high-Mg calcite in S1 to a dolomite composition in S3 (table 1).

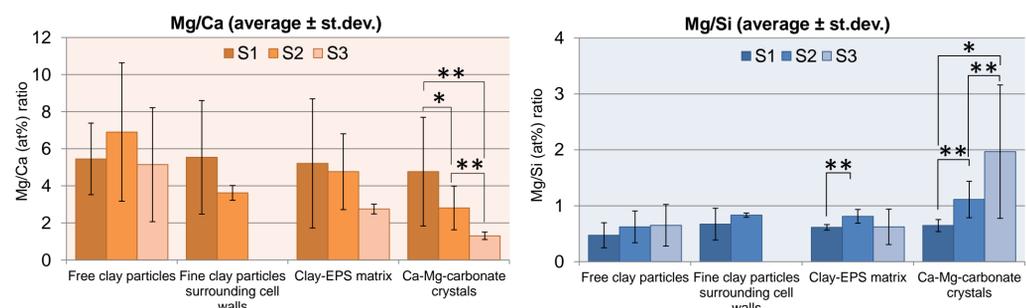


Figure 3. Average Mg/Ca and Mg/Si (atomic %) ratios (TEM-EDX of 130 independent points); * $p < 0.05$, ** $p < 0.01$.

- Significant decrease in the Mg/Ca ratio and the opposite pattern in the Mg/Si ratio in Ca-Mg carbonate crystals (fig. 3) (average \pm st.dev.):
 - Mg/Ca:** 4.8 ± 2.9 (S1) \rightarrow 2.8 ± 1.2 (S2) \rightarrow 1.3 ± 0.2 (S3),
 - Mg/Si:** 0.7 ± 0.1 (S1) \rightarrow 1.1 ± 0.3 (S2) \rightarrow 2.0 ± 1.2 (S3).
- No significant differences in the Mg/Ca and Mg/Si ratios for clay components (fig. 3).
- The 3–5-fold excess of Mg over Ca in carbonate crystals in S1 and S2 indicates that Mg may have originally been associated with clays, which act as Mg donors for incorporation into the Ca-Mg carbonate crystal lattice.

CONCLUSION

In this work, we found a transition from a predominantly high-Mg calcite composition to a dolomite composition in samples representing successive stages of phototrophic biomass drying and showed that clay minerals, along with EPS, play a significant role in the dolomitization of Ca-Mg carbonates in a hypersaline soda lake.

REFERENCES

Samylina O.S., Zaytseva L.V., 2018. Characterization of modern dolomite stromatolites from hypersaline Petukhovskoe Soda Lake, Russia. *Lethaia*. <https://doi.org/10.1111/let.12286>