Structure of cave carbonates - Mineralogical and geochemical analyses of carbonate polymorph formation processes in speleothems
Final Report

The goals of this research were to gain insights into the structure of firstly precipitating carbonates and the formation mechanism of various calcium carbonate polymorphs, to better understand the microgeochemical/microbiological environmental conditions necessary for the formation of metastable carbonates and to reveal the consequence of recrystallization and alteration via complex investigations of cave carbonates and artificially produced samples.

The project was successful from all of aspects. As a result of the complex mineralogical, petrological, geochemical and microbiological investigations we (1) identified a new nanocrystalline calcium carbonate polymorph, (2) found that bacteria living in caves produce amorphous calcium carbonate (ACC) and are able to stabilize it for a long time, (3) reported an exceptionally stable ACC produced by slime molds, (4) compared the microbiota living in various cave environments, (5) determined the geochemical character of biogenic and dominantly inorganic carbonates, (6) draw attention to the significance of the speleothems for reconstructing past climate and environmental fluctuations, (7) identified structural and morphological features suggestive of the ikaite-calcite transformation from a cryogenic cave sample, (8) performed the crystal structure characterization of calcite twins, (9) made significant progress towards understanding calcite-aragonite formation at room temperature and (10) provided insights into the ACC - ikaite - calcite transformations.

The most significant results have been published in the leading journals of geochemistry, mineralogy and petrology such as Science Advances, Scientific Reports, Plos One, Journal of Physical Chemistry C and American Mineralogist, they were reported in a book chapter and are in review in CrystEngComm. The cumulative impact factor for the published papers is 37.892. In order to point out the significance of the findings and to raise the public awareness of the topic, press materials were published at the ELKH, MTA and ELTE websites. A PhD dissertation, two MSc and a BSc thesis and two TDK essays, one of which received the first prize at the OTDK conference, were completed based on the project. The participants reported their results at national and international conferences, seminars and the two-days international "Carbonates" workshop (https://csfk.org/en/carbonates-workshop-veszprem-2022-julius-4-5/), which was organized among others to disseminate the findings of this project.

Major results

1. A monoclinic $CaCO_3$ precursor, a key player for metastable aragonite formation

The study of speleothems from the alpine Obstanser ice cave (Kartisch, Austria) led to an exciting discovery (P1). The peculiarity of this cave is the formation of metastable aragonite, which occurs in Mg-rich environments ($Mg^{2+}/Ca^{2+} > 1.5\text{-}2.0$), i.e., at conditions where aragonite abundantly precipitates. The transmission electron microscopy (TEM) investigation of the samples from the speleothems revealed a new nanocrystalline $CaCO_3$ polymorph, called mAra, which could contain up to 10 at% of Mg and precipitated prior to aragonite. Applying the state-of-the-art electron diffraction tomography method, we determined its crystal structure, found that it is crystallographically related to ordinary, orthorhombic aragonite and reported that mAra has a layered aragonite structure, in which some carbonates can be replaced by hydroxyls and up to 10 atomic % of Mg can be incorporated. Based on the new findings we proposed a mechanism of aragonite formation with mAra as the first Ca-rich carbonate phase to precipitate from water with a $Mg^{2+}/Ca^{2+} > 1.5$. We suggested that this precursor forms by incorporating Mg atoms and hydroxyl groups. During crystal growth, the mAra structure could become unstable and release Mg and hydroxyl groups to the ambient solution, thereby transforming into the closely related and more stable form of conventional orthorhombic aragonite. We proposed that mAra is a widespread crystalline $CaCO_3$ that plays a hitherto unrecognized key role in metastable aragonite formation. The new results were published in Science Advances (P1) and a Hungarian news material was posted on the MTA website (https://mta.hu/tudomany_hirei/az-aragonitkepzodes-kulcsszereplojere-bukkanhattak-magyar-olasz-es-osztrak-kutatok-109244).

2. Cave bacteria induced ACC formation

We found that microbes living on dripstone of Baradla cave produce significant amount of ACC, a precursor carbonate that has a key role in the understanding of carbonate formation and biological mineralization (P2). We observed that bacterial extracellular polymeric substance (EPS) could efficiently protect ACC from transformation, thus we managed to perform the multispectral investigation of this unusual material. We determined that the ACC-shielding EPS consisted of lipids, proteins, carbohydrates and nucleic acids. In particular, we identified large amount of long-chain fatty acid components. We suggested that ACC could be enclosed in a micella-like formula within the EPS that inhibits water infiltration. We proposed a model for ACC and calcite nucleation on the surface of bacterial cells and implied that ACC occurrence in caves can be directly linked to bacterial activity and the metastable material presumably influences the geochemical signals recorded in speleothems. The new results were published in Scientific Reports (P2) and a Hungarian news material was posted on the ELTE website (https://ttk.elte.hu/content/a-baradla-barlang-bakteriumai-segitik-a-klimakutatast.t.3400).

3. An exceptionally stable and widespread hydrated amorphous calcium carbonate precipitated by slime mold *Fuligo septica*

This work is not related to cave samples, but the results are relevant for the cave bacteria produced ACC precipitations and for understanding biogenic carbonate formations. During this study (P3) we described an exceptionally stable hydrated ACC (HACC) precipitated by the cosmopolitan slime mold *Fuligo septica* (L.) F.H. Wigg. (1780). We found that a single slime mold can precipitate up to a gram of HACC over the course of one night. X-ray powder diffraction (XRPD) patterns, TEM images, Fourier transform infrared (FTIR) spectra, together with the lack of optical birefringence indicated the occurrence of an amorphous material. XRD simulations, supported by thermogravimetric and evolved gas analysis data, were consistent with an intimate association of organic matter with ~ 1-

nm-sized ACC units that have monohydrocalcite- and calcite-like nano-structural properties. We postulated that this association imparted the extreme stability of the slime mold HACC by inhibiting loss of H_2O and subsequent crystallization. The composition, structure, and thermal behavior of the HACC precipitated by *F. septica* collected over 8000 km apart and in markedly different environments, suggested a common structure, as well as similar biochemical and biomineralization mechanisms. From the results we wrote a paper that was published in Scientific Reports (P3).

4. Calcium carbonate precipitating cultivable bacteria inhabiting different speleothems in karst caves

We investigated the microbiota of carbonate speleothems from Baradla and Csodabogyós Caves by next-generation amplicon sequencing and cultivation methods. In particular, we studied $CaCO_3$ precipitating capacity of 126 bacterial strains from different taxonomical positions at 21°C and found that 75% of the strains induced the precipitation of various calcium carbonate crystals in their colonies independently from the composition of the cell wall and EPS. We found that the mineralogical composition of the surfaces, provided for the microbial colonization, may be an important factor determining cave microbial diversity. Our analysis indicated that the precipitates were dominated by calcite, and nanosize vaterite was identified for *Paeniglutamicibacter kerguelensis* (strain BaSD-225). The study suggested that $CaCO_3$ precipitated by proteolytic bacteria are widespread in the biofilms in karst caves and these bacteria can actively contribute to $CaCO_3$ formation through alkalizing their microenvironment. From the new results we wrote a paper that was published in the Geomicrobiology Journal (P4). In addition, they were reported in an OTDK research essay (D1), which received first price, an MSc (D2) and a postgraduate thesis (D3) as well as in the PhD dissertation of Nóra Lange-Enyedi (D4).

In parallel with the microbial investigations of relatively cold caves (~ 10-11 °C) in Hungary, we also studied the microbiota from the Köröm-kút (Sajóhídvég) 78°C thermal water. We selected this place because fresh aragonite was precipitating abundantly. Next-generation amplicon sequencing methods indicated a network of diverse filamentary and/or thermophilic bacteria around the thermal well outflow of Köröm-kút. Scanning electron microscopy and X-ray diffraction investigations of the precipitates revealed the abundance of aragonite and calcite. From the results, a TDK research essay was prepared in 2022 (D5).

5. Bacterial and abiogenic carbonates formed in caves – no vital effect on clumped isotope compositions

We monitored the carbonate precipitation in the Baradla cave on a monthly basis in a place illuminated with a UV (Germicidal) lamp and in a dark (reference) place. Microbiological analyses and morphological investigations showed that the UV lamp treatment effectively reduced the number of bacterial cells, and that bacterial carbonate production strongly influenced the carbonate's morphology. Stable oxygen isotope analyses of calcite and drip waters, as well as clumped isotope measurements revealed that, although most of the studied carbonates formed close to oxygen isotope equilibrium, clumped isotope $\Delta 47$ values varied widely from equilibrium to strongly fractionated data. The conclusion of this study was that although the morphology of carbonates precipitated in bacteria-poor (dominantly inorganic) and bacteria-rich (organic) environments significantly differed, there was no significant difference between the geochemical characters of the two carbonate types. The new results were published in Plos One (P5) and a Hungarian news material was posted on the ELKH website (https://elkh.org/hirek/bakteriumok-mindenhol-a-cseppkokepzodes-mechanizmusanak-ujszeru-vizsgalata-a-foldtudomany-a-mikrobiologia-es-a-fizika-kutatoinak-osszefogasaval/).

6. Monitoring and geochemical investigations of caves in Hungary: implications for climatological, hydrological and speleothem formation processes

The monitoring activities in Hungarian caves including the Béke and Baradla caves in the Aggtelek Karst revealed that the speleothems are able to record temperature and hydrological changes, and hence the measured trace element and isotopic compositions together with petrographic characteristics permit to reconstruct past climate and environmental fluctuations. In addition, the equations that best describe the carbonate-water oxygen isotope fractionation and best reflect the temperature dependence of the isotopic composition of precipitations were identified for paleotemperature reconstruction. The new data have been published as a book chapter for „Cave and Karst Systems of Hungary" (P6).

7. Tracing structural relicts of the ikaite to calcite transition from a cryogenic cave sample

This study (P7) was induced by the ANN 141894 bilateral project. The target of this investigation was a cryogenic carbonate sample from Victoria Cave, Russia. However, the findings are also relevant to this project, therefore, the main results are reported here. We investigated the nanostructure of 25,000-43,000-year-old glendonite, a calcite ($CaCO_3$) pseudomorph after ikaite ($CaCO_3 x 6H_2O$), from Victoria cave (Southern Ural, Russia) with a combination of methods in search of structural features indicative of the ikaite-to-calcite transformation. The importance of this work was that glendonites are commonly used as paleoclimatological indicators for inferring temperatures close to freezing point. Our study, published in American Mineralogist (P7), suggested that the aligned mesopores, frequently occurring twins, small grain size, presence of aqueous inclusions and the observed porosity arise from the ikaite-to-calcite transformation and thus may be used as criteria for the former presence of ikaite and hence for cold paleotemperatures. However, since similar features might also be common in biogenic carbonates, the diagnostic macroscopic pseudomorphs after ikaite are equally important for identifying glendonites and inferring cryogenic conditions.

8. Diffraction features from (10$\bar{1}$4) calcite twins mimicking crystallographic ordering

During the TEM characterization of the crystal structure of the samples from the Victoria cave, it was found that the diffraction characteristics of the calcite crystals are the same as the structural features previously attributed to the Mg-Ca arrangement in the literature (P8). Since the sample was pure calcium carbonate, practically free of contaminants, Mg arrangement was not possible. The detailed crystal structure analysis revealed that $(10\bar{1}4)$ calcite twins and the orientation change of the carbonate groups across the twin interface were clearly responsible for the appearance of the reflections observed in the diffraction patterns. The importance of this work, published in Minerals (P8), is that it draws attention to the correct interpretation of diffraction patterns, i.e., considering the occurrence of $(10\bar{1}4)$ twins before the conclusion of the structural arrangement in calcite.

9. Calcite/aragonite epitaxy

Since the originally proposed ab initio calculations did not provide useful information about understanding carbonate formation, we turned toward calculating the stable interface between aragonite and calcite. This study was prompted by the TEM results of cryogenic cave carbonates, which indicated a possible competitive growth process between calcite and aragonite. With our Italian collaborators we analyzed several calcite and aragonite epitaxial and relaxed interfaces and found a hexagonal $CaCO_3$ polymorph that corresponded to the phase (called hexarag) recently identified during the molecular dynamic study on the high-temperature (600K) aragonite-calcite transition. Our study indicated that this phase can also form at low temperature and has implications for understanding the sluggish mechanisms of aragonite-calcite transformation at ambient conditions. The new results were published in the Journal of Physical Chemistry C (P9).

10**. Insights into the amorphous calcium carbonate (ACC) → ikaite → calcite transformations**

Much effort has been expanded to prepare crystalline precursor carbonates and thus to better understand carbonate crystallization. We focused on the synthesis of ACC as well as ikaite ($CaCO_3 \cdot 6H_2O$). This hydrous crystalline carbonate is expected to have a key role in cryogenic carbonate precipitation. Of particular interest is the finding of two ACC types (referred to as I and II) that differ not only in their morphology, particle size, water content and stability but in their mode of formation. We showed the occurrence of the crystalline precursor ACC (I) and the ACC (II) formed from a crystalline material. The spherical 100 nm sized ACC (I) formed below 5 °C aged to micron-sized ikaite ($CaCO_3 \cdot 6H_2O$). However, laboratory-controlled ikaite dehydration by organic solvents and vacuum pumping at room temperature and by increasing the temperature from 5 to 30 °C within one-minute resulted in ACC (II) before the formation of the thermodynamically stable calcite. Temperature-dependent investigation performed between 25 and 350 °C indicated that ACC (I) was more stable than ACC (II) despite its higher water content and at 300 - 350 °C ACC (I) could be dehydrated to an amorphous material containing 0.03 mol water. We suggested that the different ACC types could be attractive for material science applications, and the finding of an amorphous phase during the ikaite → calcite transition implies the alteration of the original geochemical signal. From the new results we prepared a manuscript, which is in review in CrystEngComm (submission date 19/10/2022) (P10). In addition, they were reported in an OTDK research essay (D6) and an MSc thesis (D7).

Use of the project results

Our new results are of fundamental interest for understanding calcium carbonate (trans)formation and biomineralization. The findings are relevant for getting insights into the structure and formation mechanisms of firstly precipitating carbonates. Since the transformation of carbonates alters the geochemical data preserved in the original carbonates, our research is important for reconstructing past climate. The targeted preparation of ACC, studied during this project, can aid in the synthesis of additive-free carbonates for drug delivery systems and for heavy and toxic elements removal. The findings aid toward controlling/engineering the nucleation and growth of calcium carbonates and contribute to better understanding the crystallization process of ACC.

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Papers (participants of the project in bold)

P1. **Németh, P;** Mugnaioli, E; Gemmi, M; **Czuppon, Gy;** Demény, A; Spötl, C (2018) A nanocrystalline monoclinic $CaCO_3$ precursor of metastable aragonite**.** SCIENCE ADVANCES 4: 12 Paper: eaau6178. DOI: 10.1126/sciadv.aau6178 *IF: 12.804.*

P2. **Enyedi, N**; **Makk, J**; **Kótai, L**; **Berényi, B**; Klébert, Sz; Sebestyén, Z; Molnár, Zs; **Borsodi, AK**; **Leél-Őssy, Sz**; Demény, A, **Németh, P** (2020) Cave bacteria-induced amorphous calcium carbonate formation. SCIENTIFIC REPORTS 10: 1 Paper: 8696. DOI: 10.1038/s41563-020-0759-8 *IF: 4.379.*

P3. Garvie, LAJ; **Németh, P**; Trif, L (2022) An exceptionally stable and widespread hydrated amorphous calcium carbonate precipitated by the dog vomit slime mold Fuligo septica (Myxogastria). SCIENTIFIC REPORTS 12: 1 Paper: 3642. DOI: 10.1038/s41598-022-07648-9 *IF: 4.996.*

P4. **Lange-Enyedi, N**; **Németh, P**; **Borsodi, AK**; Halmy, R; **Czuppon, Gy**; Kovács, I; **Leél-Őssy, Sz**; Demény, A; **Makk, J** (2022) Calcium Carbonate Precipitating Cultivable Bacteria from Different Speleothems of Karst Caves. GEOMICROBIOLOGY JOURNAL 39: 2 (107-122). DOI: 10.1080/01490451.2021.2019857 *IF: 2.412.*

P5. Demény, A; Rinyu, L; **Németh, P**; **Czuppon, Gy**; **Enyedi, N**; **Makk, J**; **Leél-Őssy, Sz**; Kesjár, D; Kovács, I (2021) Bacterial and abiogenic carbonates formed in caves–no vital effect on clumped isotope compositions. PLOS ONE 16: 1 Paper: e0245621. DOI: 10.1371/journal.pone.0245621 *IF: 3.240.*

P6. **Czuppon, Gy**; Demény, A; **Leél-Őssy, Sz**; Stieber, J; Óvári, M; Dobosy, P; Berentés, Á; Kovács, R (2022) Monitoring and Geochemical Investigations of Caves in Hungary: Implications for Climatological, Hydrological, and Speleothem Formation Processes In: Veress, M; **Leél-Őssy, Sz** (eds.) Cave and karst systems of Hungary; Springer International Publishing (Cham, Switzerland) 465-486.

P7. **Németh, P**; Töchterle, P; Dublyansky, Y; Stalder, R; Molnár, Zs; Klébert, Sz; Spötl, C (2022) Tracing structural relicts of the ikaite-to-calcite transformation in cryogenic cave glendonite. AMERICAN MINERALOGIST 107 Paper: 1960-1967. DOI: 10.2138/am-2022-8162 *IF: 3.066.*

P8. **Németh, P** (2021) Diffraction Features from $(10\bar{1}4)$ Calcite Twins Mimicking Crystallographic Ordering. MINERALS 11: 7 Paper: 720. DOI: 10.3390/min11070720 *IF: 2.818.*

P9. Bruno, M; Prencipe, M; Aquilano, D; Cotellucci, A; Ghignone, S; **Németh, P** (2022) Calcite/Aragonite Epitaxy: A Computational Study for Understanding Mollusk Shell Formation. JOURNAL OF PHYSICAL CHEMISTRY C 126: 14 (6472-6481). DOI: 10.1021/acs.jpcc.2c00785 *IF: 4.177.*

P10. **Lázár, A;** Molnár, Zs; Demény, A; **Kótai, L**; Trif, L; **Béres, KA**; Bódis, E; Bortel, G; Aradi, LE; Karlik, M; Szabó, MZ; Pekker, Á; Németh, G; Kamarás, K; Garvie, LAJ; **Németh, P** Insights into the amorphous calcium carbonate (ACC) → ikaite → calcite transformations. Submitted to CRYSTENGCOMM (*IF: 3.756*) on 19/10/2022.

Dissertations, thesis and essays (participants of the project in bold)

D1. Halmy R. (2019) Carbonate-forming bacteria from Csodabogyós Cave. OTDK research essay (In Hungarian), Department of Microbiology, Eötvös Loránd University, 40 p.

D2. Halmy R. (2019) Carbonate-forming bacteria from Csodabogyós Cave. MSc thesis work (In Hungarian), Department of Microbiology, Eötvös Loránd University, 80 p.

D3. Halmy R. (2021) Investigation of the carbonate precipitation conditions of bacterial strains from Csodabogyós cave. Postgraduate thesis (In Hungarian), Department of Microbiology, Eötvös Loránd University, 49 p.

D4. **Lange-Enyedi NT.** (2022) Analysis of biogeochemical processes involving microorganisms in Hungarian karst systems. PhD dissertation (In Hungarian), Department of Microbiology, Eötvös Loránd University, 151 p. Submitted to the PhD committee on 31/08/2022.

D5. Németh Á. Cs. (2022) Mineralogy and microbial diversity of the microbialites in a Hungarian thermal well water (Köröm, Hungary). TDK research essay, Department of Microbiology, Eötvös Loránd University, 28 p.

D6. **Lázár A.** (2021) Investigation of ikaite (calcium carbonate hexahydrate) – amorphous calcium carbonate transformation. OTDK research essay (In Hungarian), Research Institute of Biomolecular and Chemical Engineering, University of Pannonia, 37 p.

D7. **Lázár A.** (2021) Preparation of ikaite (calcium carbonate hexahydrate) and investigation its transformation process. MSc thesis work (In Hungarian), Research Institute of Biomolecular and Chemical Engineering, University of Pannonia, 52 p.

Abstract and talks for seminars, conferences and the "Carbonate" workshop (participants of the project in bold)

A1. **Berényi B., Kótai L., Czuppon Gy.,** Demény A., Kesjár D., Kovács I., **Makk J., Enyedi NT**, **Leél- Őssy Sz., Szieberth D., Németh P.** Synthesis of cave carbonates (In Hungarian). Oral presentation at 13th Winter School in Mineral Sciences, Veszprém, Hungary, 19.01.2018.-20.01.2018.

A2. **Enyedi NT., Németh P., Borsodi A., Czuppon Gy., Leél-Őssy Sz., Berényi B., Makk J.** Bacterial influence in the formation of cave carbonates. (In Hungarian). Oral presentation at 13th Winter School in Mineral Sciences, Veszprém, Hungary, 19.01.2018.-20.01.2018.

A3. **Czuppon Gy.,** Kovács Zs., Óvári M., John Sz., **Berényi B.,** Kesjár D., Kovács I., Demény A., **Makk J., Enyedi N. T., Leél- Őssy Sz., Németh P.** Determining factors in the formation of cave carbonates in Csodabogyós cave. (In Hungarian). Oral presentation at 13th Winter School in Mineral Sciences, Veszprém, Hungary, 19.01.2018.-20.01.2018.

A4**. Enyedi N., Németh P., Borsodi A., Czuppon Gy., Berényi B.,** Leél-Őssy Sz., Óvári M., Dobosy P., **Makk J.** Calcium-carbonate precipitating bacteria from Baradla Cave (In Hungarian). Oral presentation at Congress of the Hungarian Society for Microbiology (2018) and 13th Fermentation Colloquium. Eger, Hungary, 17.10.2018.-19.10.2018.

A5. **Németh P.**, Mugnaioli E., Gemmi M., **Czuppon Gy.,** Demény A., Spötl C. A new nanocrystalline $CaCO_3$ polymorph, a key player for the formation of metastable aragonite. Oral presentation at European Geophysical Union, Vienna, Austria, 09.04.2019.

A6. **Németh P.,** Mugnaioli E., Gemmi M., **Czuppon Gy.,** Demény A., Spötl C. Monoclinic aragonite, the precursor of metastable aragonite formation. (In Hungarian). Oral presentation at conference of Hungarian Society for Microscopy Siófok, Hungary, 23.05.2019-25.05.2019.

A7. **Enyedi NT., Makk J., Berényi B., Kótai L., Czuppon Gy.,** Klébert Sz., Borsodi A., **Leél-Őssy Sz.,** Demény A., **Németh P.** Study of the bacterial induced carbonate precipitation (In Hungarian). Oral presentation at 14th Winter School in Mineral Sciences, Veszprém, Hungary, 18.01.2019-19.01.2019.

A8. **Németh P.,** Mugnaioli E., Gemmi M., **Czuppon Gy.,** Demény A., Spötl C. A new $CaCO_3$ polymorph (mAra) from the Obstanser ice cave, Oral presentation at 14th Winter School in Mineral Sciences, Veszprém, Hungary, 18.01.2019-19.01.2019.

A9**. Enyedi NT.,** Borsodi A., **Németh P.,** Felföldi T., Szabó A., **Berényi B., Kótai L.,** Dobosy P., **Makk J.** Geomicrobiological study in a carbonate cave of the Aggtelek Karst, Hungary. Oral presentation at 18th International Congress of the Hungarian Society for Microbiology Conference, Budapest, Hungary, 03.07.2019-05.07.2019.

A10. **Enyedi NT.,** Halmy R., **Borsodi A., Németh P., Czuppon Gy., Berényi B.,** Kovács I., Leél-Őssy Sz., **Makk J.** Calcium-carbonate precipitating bacteria from Csodabogyós Cave. Poster at 18th International Congress of the Hungarian Society for Microbiology Conference, Budapest, Hungary, 03.07.2019-05.07.2019.

A11**. Berényi B, Kótai L, Enyedi NT, Makk J,** Domján A, Trif L, Szieberth D, Molnár Zs, Klébert Sz, Sebestyén Z, Sajó I **Németh P.** What is the precursor of crystalline carbonates? (In Hungarian). Oral presentation at 15th Winter School in Mineral Sciences, Veszprém, Hungary,17.01.2020.-18.01.2020.

A12. **Enyedi NT., Németh P., Borsodi A., Czuppon Gy., Berényi B.,** Kovács I., Felföldi T., Spötl C., **Makk J.** Extremophilic bacteria from karst cave environments (In Hungarian). Current Research of Environmental Sciences in the Carpathian Basin. Budapest, Hungary, 04.06.2020.-06.06.2020.

A13. **Németh P.** Investigation of carbonate polymorph formation processes in speleothems and synthetic materials (In Hungarian). Online presentation at "ÚNKP" Conference 2019/2020, Veszprém, Hungary 24.06.2020.

A14. **Enyedi, NT.** Diversity and carbonate precipitation ability of ice cave bacterial communities (in Hungarian). Online presentation at "ÚNKP" Conference 2019/2020, Budapest, 14.12.2020.

A15. **Lázár A.,** Molnár Zs., Aradi LE., **Kótai L.,** Klébert Sz., Trif L., Bódis E., **Németh P.** Investigation of ikaite (calcium carbonate hexahydrate)-ACC (amorphous calcium carbonate) transformation process (In Hungarian). Online presentation at "PhD hallgatók anyagtudományi napja XX.", Veszprém, Hungary, 16.11.2020.

A16. **Németh P., Lange-Enyedi NT., Makk J., Kótai L.,** Klébert Sz., Sebestyén Z., Molnár Zs., Borsodi A., **Leél-Őssy Sz.,** Demény A. Bacterial amorphous calcium carbonate. Oral presentation at 16th Winter School in Mineral Sciences, Veszprém, Hungary, 22.01.2021.-23.01.2021.

A17**. Lange-Enyedi NT., Németh P.,** Borsodi A., **Czuppon Gy.,** Kovács I., Felföldi T., Spötl C., **Makk J.** Carbonate precipitating bacteria from an Austrian ice cave. Oral presentation at 16th Winter School in Mineral Sciences, Veszprém, Hungary, 22.01.2021.-23.01.2021.

A18**. Lázár A.,** Molnár Zs., Aradi LE., **Kótai L.,** Klébert Sz., Trif L., Bódis E., **Németh P.** The conversion of ikaite (calcium carbonate hexahydrate) into amorphous calcium carbonate (In Hungarian). Oral presentation at 16th Winter School in Mineral Sciences, Veszprém, Hungary, 22.01.2021.-23.01.2021.

A19. **Lange-Enyedi NT., Németh P.,** Borsodi A., **Czuppon Gy.,** Kovács I., Felföldi T., Spötl C**., Makk J.** Geomicrobiological study of bacteria inhabiting an ice cave (In Hungarian). Oral presentation at 16th Carpathian Basin Conference for Environmental Sciences. Budapest, Hungary, 30.03.2021.-01.04.2021.

A20. **Németh P.** Diffraction artefacts from cryogenic calcite twins (In Hungarian). Online presentation at conference of Hungarian Society for Microscopy, Hungary, 13.05.2021.

A21. **Lange-Enyedi NT.** Bacterial carbonate precipitation at low temperature (In Hungarian). Online presentation at "ÚNKP" Conference 2020/2021, Budapest, 31.08.2021.

A22. **Németh P.** Investigation of carbonate polymorph precipitation processes in speleothems and synthetic materials (In Hungarian). "ÚNKP" Conference, Veszprém, Hungary 13.10.2021.

A23. **Lázár A.**, Aradi LE., Bortel G., Demény A., Kamarás K., Karlik M., Molnár Zs., Németh G., Pekker Á., Szabó MZ., Trif L., **Németh P.** Transformations of metastable calcium carbonate modifications under controlled conditions (In Hungarian). Online presentation at 17th Winter School in Mineral Sciences, Veszprém, Hungary, 28.01.2022.-29.01.2022.

A24. **Lázár A.,** Molnár Zs., Aradi LE., **Kótai L.,** Demény A., Klébert Sz., Trif L., Bódis E., **Németh P.** Metastable calcium carbonate modifications formed at cryogenic temperature (In Hungarian). Oral presentation at XXVI. Bolyai Conference, Budapest, Hungary, 09.04.2022.-10.04.2022.

A25. **Németh P**. What can we learn by studying calcium carbonates by electron microscopy? (In Hungarian) Oral presentation at CSFK 10 symposium. Budapest, Hungary, 20.04.2022

A26. **Lange-Enyedi NT., Makk J., Kótai L.,** Klébert Sz., Sebestyén Z., Molnár Zs., **Borsodi A., Leél-Őssy Sz.,** Demény A. **Németh P.** Amorphous calcium carbonate precipitation by cave bacterial strains (In Hungarian). Oral presentation at conference of Hungarian Society for Microscopy, Siófok, Hungary, 05.05.2022-07.05.2022.

A27. **Lázár A.**, Aradi LE., Bortel G., Demény A., Kamarás K., Karlik M., Molnár Zs., **Kótai L.** Németh G., Pekker Á., Szabó MZ., Trif L., **Németh P**. Transformations of metastable calcium carbonate modifications under controlled conditions (In Hungarian). Oral presentation at conference of Hungarian Society for Microscopy Conference Siófok, Hungary, 05.05.2022-07.05.2022.

A28. **Lange-Enyedi NT.** Microbially induced carbonate precipitation in cave environments. Oral presentation at Carbonate workshop, Veszprém, Hungary, 04.07.2022-05.07.2022.

A29. **Lázár A.,** Demény A., Bortel G., Trif L., Karlik M., Szabó MZ., Molnár Zs. **Németh P.** Transformations of metastable calcium carbonate modifications under controlled condition. Oral presentation at Carbonate workshop, Veszprém, Hungary, 04.07.2022-05.07.2022.24.

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