

Carbonate workshop program

Monday (04.07.2022)				
9:55	10:00	Péter Németh	Workshop opening	
Carbonate fabrics in various geological environments				
10:00	10:25 (20 min speech+5 min discussion)	Adrian Immenhauser	Carbonate fabrics: A curiosity-driven journey from caves to the burial domain	Carbonate fabrics (including morphology, mineralogy, crystallography and geochemistry) yield very significant, albeit complex, information regarding the nucleation, precipitation and alteration processes of Ca/MgCO ₃ . Remarkably, after more than 100 years of research, many very general questions remain unresolved and longstanding paradigms are questioned. In the context of a journey from the cave to the burial environment, some outstanding aspects of helictite (eccentrics etc.), cryogenic calcite and saddle dolomite fabrics are documented and discussed. The approach chosen makes use of a careful documentation of natural depositional environments, combined with state-of-the-art precipitation experiments and optical and geochemical analytical tools.
10:25	10:50 (20 min speech+5 min discussion)	Silvia Frisia, Andrea Borsato, Péter Németh, Attila Demény, Béla Pécz, Péter Pekker	Crystallization pathways in tropical and polar carbonates	Fabrics of layered continental carbonates depend to varying degrees on crystallization processes, which in-turn are influenced by metabolic processes and the presence in the parent fluid of natural organic compounds. In caves of the Tropical Cook Islands (South Pacific) we have documented shifts between layer growth and nanoparticle/nanocrystal attachment. Nanoparticles predominantly consist of Amorphous Calcium Carbonate (ACC) and nanocrystals are composed of calcite. We suggest that these shifts are indicative of both classical and non-classical growth influenced by high calcite supersaturation and presence of natural organic compounds. Presence of organics (both dissolved organic matter and colloids) appear to stimulate preferential incorporation of nanoparticles as non-monomer species (non-classical). Subsequent „incorporation” of the ACC nanoparticles into the large calcite substrate seemingly occurs via dissolution-reprecipitation. We also documented the formation of nanoparticles of amorphous silica which, however, do not appear to be incorporated in the final speleothem calcite columnar crystals. By contrast, black subglacial crusts consisting of large, elongated columnar crystals that formed in Antarctica incorporate amorphous silica spherules that show different degrees of diagenetic alteration. The large, black columnar calcite crystals are also characterized by multiple twinning. We speculate that twinning is due to growth processes, rather than stress. The black crystals are, thus, more akin to calcite known to form through biomineralization than that formed at high temperature or during metamorphism. Another finely crystalline, white subglacial crust closely associated with till appears to consist exclusively of calcite and preliminary observations did not reveal defects. We infer that this white calcite formed from a „gel-like”, highly supersaturated solution during freezing of the basal ice and, as such, there is no clear influence of microbial processes (or of organic compounds) in its formation.
10:50	11:10 (15 min speech+5 min discussion)	Attila Demény, Silvia Frisia, Andrea Borsato, Péter Németh, Béla Pécz, Péter Pekker	Formation conditions of Antarctic subglacial calcites	Subglacial calcites of earlier collections were studied by means of fluorescence microscopy, scanning and transmission electron microscopy, and conventional stable isotope and clumped isotope mass spectrometry. Although earlier studies assumed the possibility of hydrothermal carbonate formation, clumped isotope data suggest precipitation around 0 °C. Nanometer-sized silica globules within the enigmatic Elephant Moraine black calcite were detected by transmission electron microscopy and indicate the presence of dissolved carbonate and Si in the parent solution. Stable H and O isotope compositions of fluid inclusion hosted waters indicate different fluid generations. These observations collectively suggest mixing of different fluids, either related to glacial meltwater migrations, or mixing of meltwater and a solution that had undergone fluid-rock interaction.
11:10	11:30	coffee break		

Cryogenic carbonates				
11:30	11:40 (5 min speech+ 5 min discussion)	Yuri Dublyansky , Christoph Spötl, Gabriella Koltai	Cryogenic cave carbonates: current research and open questions	Cryogenic cave carbonates (CCC) exhibit a large variety of morphologies, including pseudomorphs, and show characteristic trends in O and C stable isotopes. These features are controlled primarily by the crystallization kinetics. Calcite is the dominant phase; aragonite and ikaite have also been reported from natural caves.
11:40	11:50 (5 min speech+ 5 min discussion)	Christoph Spötl , Gabriella Koltai, Yuri Dublyansky, Peter Németh	Growing cryogenic carbonates in an Alpine ice cave	In recent years so-called coarse-grained cryogenic cave carbonates have gained increasing attention as evidence of past glaciation episodes in caves. While geochemical parameters provide some insights into how they formed, no study has documented their formation in statu nascendi. During winter 2021/22 we conducted freezing experiments in an Alpine ice cave and grew these cryogenic carbonates under controlled conditions. We will share first results of this ongoing work.
11:50	12:400 (5 min speech+ 5 min discussion)	Gabriella Koltai , Christoph Spötl, Yuri Dublyansky	Cryogenic cave carbonates in paleoclimate research	Coarse crystalline cryogenic cave carbonates (CCC for short) form via freezing-induced supersaturation of small water bodies within cave ice. Currently CCCs are the best and sometimes single evidence for former glaciation of caves. Their age can be quite accurately determined and thus they can be used to reconstruct the time when ice was present in a particular cave section all year round. Here we share an example from an alpine cave.
12:00	12:15 (10 min speech+ 5 min discussion)	Péter Németh , Christoph Spötl, Gabriella Koltai, Yuri Dublyansky, Zsombor Molnár Péter Pekker	Tracing transformation relicts in cryogenic cave carbonates	Cryogenic cave carbonates are unique cave deposits that can be associated with the former presence of permafrost. However, the reliability of geochemical signature derived from these unique deposits requires the knowledge of initial carbonate phase/s and their transformation process. In our presentation we investigate the nanostructure of cryogenically formed carbonates and look for the precursor carbonate phases and traces of transformation.
12:15	12:30 (10 min speech+ 5 min discussion)	Rastislav Milovský , Monika Orvošová, HongChun Li, Stanislava Milovská, Andrea Schröder-Ritzrau, Michael Deininger, Pavel Herich, Juraj Šurka	Dating issues in cryogenic calcites from caves in Slovakia	Caves in mountain areas of Slovakia are rich in cryogenic phenomena including CCC. Aiming to relate the CCC ages to climatic events we dated them in several caves. Their ages range from 12.08 to 47.6 ka BP, with unique time span in each cave. In compliance with theory of their formation during thawing of permafrost, we expected the ages to coincide with interstadials; however, the correlation is very dubious: some ages fit into warm periods while others into cold ones. In order to resolve the expected effect of depth to the delay of the CCC crystallization we dated them in several cave halls at different depths of one cave system (Zlomiská cave, Nízke Tatry Mts.), and even particular morphotypes within CCC populations, whose crystallization successions are reliably determined by overgrowing rule and stable isotopes. Again, the results widely scattered with age spans of 0.47 to 16.49 ka, and in some successions the ages were inversely related to depth. Two possible solutions emerge: either the theory of CCC formation needs revision, or there is a problem with dating. To move further we now investigate 1. how the age-mismatch relates to the cave-surface distance and size of hall; 2. how trace elements fractionate along growth successions.
12:30	12:40 (5 min speech+ 5 min discussion)	Monika Orvošová , Stanislava Milovská, Rastislav Milovský, Adrian Biroň	Metastable cryogenic carbonates from caves in Slovakia	We present our research of seasonal fine cryogenic cave carbonates (CCCfine) as a specific type of speleothems, whose precipitation is triggered by freezing of mineralized karst water directly in cave. Their formation is influenced by kinetic isotopic fractionation during rapid freezing. In recently formed CCCfine in permanently or seasonally frozen caves, we have identified rare assemblages of metastable carbonates: i) ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) + calcite \pm lansfordite ($\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$), bound to seasonal glaciation of entrance areas of the caves; ii) lansfordite + ikaite \pm nesquehonite ($\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2\text{H}_2\text{O}$) \pm calcite, and calcite + monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) that occur in periglacial zones inside the cave halls. We have also described and defined a so far unknown, transitional type of CCC and at the same time a new genetic type of speleothem – cryogenic cave pearls, which are globally rare.
12:50	13:50	lunch break		

Calcium carbonate precursors and synthesis I

13:50	14:15 (20 min speech+ 5 min discussion)	Enrico Mugnaioli	Structure characterization of CaCO ₃ in early formation stages by 3D electron diffraction	Automatic systems for 3D data acquisition and analysis have turned electron diffraction into a reliable method for structure characterization of sub-micrometric crystalline domains. Here we will show the application of this technique for the analysis of mArA, a modulated precursor of aragonite able to incorporate small quantities of Mg and sampled directly from drip water inside the Obstanzer Eishöhle cold cave, Austria. Electron diffraction can be nowadays considered a mature method for the systematic characterization of carbonate crystalline seeds.
14:15	14:40 (20 min speech+ 5 min discussion)	Martin Dietzel	Consequences of amorphous precursors on elemental and isotope composition of crystalline CaCO ₃	Elemental and isotope signals of CaCO ₃ minerals are frequently used as proxies to reconstruct the (paleo)environmental conditions during their formation. As amorphous calcium carbonate (ACC) is known to be an important precursor for crystalline carbonates, these proxy signals have to be evaluated by considering the individual CaCO ₃ formation pathways, as well as reaction kinetics vs. equilibrium approaches. The elemental and isotope fractionation between ACC / crystalline CaCO ₃ and the precipitating solution are discussed with respect to ion exchange behavior and metastability / precipitation rate and open vs. closed transformation conditions.
14:40	14:50 (10 min speech+ 5 min discussion)	Anett Lázár , Attila Demény, Gábor Bortel, László Trif, Máté Karlik, Máté Zoltán Szabó, Zsombor Molnár, Péter Németh	Transformations of metastable calcium carbonate modifications under controlled conditions	Amorphous calcium carbonate (ACC) is a precursor of ikaite (calcium carbonate hexahydrate), a carbonate mineral that forms under cryogenic conditions. In our presentation we investigate the laboratory-produced ikaite-ACC-calcite transformation process and compare the morphology, stability, and water content of the starting (as-synthesized) and the ikaite-transformed ACC.
14:55	15:10 (10 min speech+ 5 min discussion)	Kende Attila Béres , Anett Lázár, Péter Németh, László Kótai	Does calcium pyrocarbonate exist?	Knowing the transformation process of calcium carbonate modifications is essential for understanding the geochemical signature preserved in carbonate sediments. According to literature data there is a Ca acid carbonate that is characterized by unprecedentedly high CO ₂ (Ca/CO ₂ = 2.8) content. This enigmatic composition may be explained by the mixture of CaC ₂ O ₅ (pyrocarbonate) and Ca(HC ₂ O ₅) ₂ (hydrogen pyrocarbonate). The aim of our research is to synthesize and characterize these compounds. Since they are highly metastable, we also look for the pyrocarbonate anions in the similar Co system.

15:10 15:30 **coffee break**

Calcium carbonates precursors and synthesis II

15:30	15:45 (10 min speech+ 5 min discussion)	Jean-Michel Brazier , Katja Goetschl, Martin Dietzel, Vasileios Mavromatis	Incorporation of trace elements in aragonite: a window to new proxies	The chemical and isotope compositions of carbonate minerals give a fantastic opportunity to rebuild the composition of the reactive solution from which they were formed and are thus of first importance for paleoenvironmental reconstruction throughout geological time. In this regard, the character, quantification and reaction mechanisms of trace element incorporation into carbonate minerals were widely studied over the last five decades. Deciphering the effect of a single physical or chemical parameter on the incorporation of traces in natural CaCO ₃ is, however, not straightforward. Systematic experimental studies under highly controlled physicochemical conditions can provide fundamental understanding of how to assess and make use of these chemical signatures as environmental proxies. This presentation will focus on the experimental incorporation of Zn, Ni, Co, Mg and Li ions into aragonite. These five elements are incompatible with the aragonite crystal structure and thus show very low values of distribution coefficient between aragonite and the reactive solution. Nevertheless, these experimental values are highly valuable and open the doors to a wider and more accurate use of aragonite as a paleoenvironmental archive.
-------	---	---	---	--

15:45	16:00 (10 min speech+ 5 min discussion)	Katja E. Goetschl , Martin Dietzel	In-situ monitoring of CaCO ₃ precipitation reactions in aqueous solution under precisely defined physicochemical conditions	Calcium carbonate (CaCO ₃) minerals occur in large quantities and varieties in technical and in natural environments on the Earth's surface. Parameters like the chemical composition of the precipitating fluid, pH, temperature and pressure strongly control the resulting CaCO ₃ polymorph but also its chemical and isotopic composition as well as its structural ordering and shape. During the last two decades, a large body of studies was assigned to investigate the formation of CaCO ₃ minerals via amorphous and metastable precursors. In order to mechanistically decipher and assess the parameters controlling the structure and elemental composition of a precipitating CaCO ₃ mineral via an amorphous precursor we designed an experimental set-up where we can precisely define physicochemical conditions during CaCO ₃ formation. In-situ mineralogical characterization using Raman spectroscopy together with pH monitoring, chemical analyses of the solution and geochemical modeling allow us to unravel the complex interplay between solid and solution at the time of mineral (trans)formation. Results of experimental studies will be discussed which improve our current understanding on CaCO ₃ mineral formation mechanisms, polymorph developments and chemical signatures of the precipitated minerals.
16:00	16:15 (10 min speech+ 5 min discussion)	Stefanie Eichinger , Ronny Boch, Katja Götschl, Robert Wenighofer, Renè Hoffmann, Cyrill Grengg, Andre Baldermann, Robert Galler, Adrian Immenhauser, Martin Dietzel	Subsurface low Mg-calcite-aragonite formation – Field based experiments and in-situ monitoring in the Erzberg mine (Austria)	The iron ore deposit Erzberg (Austria) is dominated by diverse Fe and Ca rich carbonate minerals of hydrothermal origin (e.g., siderite and ankerite). However, recent discoveries made at a historic sub-surface mining site have identified geologically young carbonate mineralizations rich in Mg and Ca (< 150 years), which precipitate from discharging groundwater at low temperature. An active precipitation site was thus chosen as a modern, natural laboratory in order to investigate the formation of aragonite – low Mg calcite mineral sequences, which are frequently observed in fractures and faults of the Erzberg mountain range, i.e., as secondary vein infillings and as flowstones. To get insights into the individual CaCO ₃ formation mode(s), the aqueous solution composition as well as local atmosphere were monitored based on repeated sampling campaigns and automated water and air data loggers. Further, on-site experiments were carried out by exposing calcite and aragonite seed crystals to discharging groundwater to induce secondary CaCO ₃ precipitation. The Ca-carbonate precipitates from natural deposition and on artificial substrates were characterized by mineralogical, chemical and microstructural techniques. Preliminary results indicate a preferential nucleation and crystal growth of low Mg calcite, followed by aragonite precipitation at available surface sites of these newly formed low Mg calcite crystals at 5.5 ± 0.6 °C and pH 7.4 to 8.1. This supports results obtained from cathodoluminescence, where aragonite typically precipitates in fascicular shapes starting from a certain (passivated) low Mg calcite surface site, simultaneously to ongoing calcite precipitation at still active growth sites. We attribute this to local calcite growth inhibition under high aqueous molar Mg/Ca ratios (~1 to 2), i.e., causing 'Mg poisoning' and thus changes in CaCO ₃ polymorphism. Variation of pH and coupled Mg/Ca ratios are primarily controlled by local host rock weathering, enhanced CO ₂ degassing and CaCO ₃ precipitation kinetics, as well as by the varying flow rate conditions depending on seasonality and interaction of the subsurface with the atmosphere outside. This natural laboratory reveals prominent and recurrent calcite-aragonite formation being controlled by distinct cyclic environmental changes, which induce solid-liquid-gaseous gradients and nano-to-micron-scale fluid-rock/mineral interface reactions that impact the dependencies of different Ca-carbonate polymorphs.
16:15	16:30 (10 min speech+ 5 min discussion)	Michael Wedenig , Ronny Boch, Albrecht Leis, Martin Dietzel	Modulating CaCO ₃ precipitation rate, crystal structure and morphology by polyaspartate	Polyaspartic acid (PAsp) is a bio-inspired polymer that mimics the structure of naturally occurring polypeptides. Today PAsp is manufactured in large industrial quantities and respective commercial products are used to inhibit and modulate CaCO ₃ precipitation in diverse technical settings. The properties of individual PAsp-products regarding inhibition performance and effect on crystal shape modulation were assessed by CaCO ₃ precipitation experiments using in-situ monitored CO ₂ degassing technique at distinct PAsp concentrations and degassing/precipitation rates. Thermodynamic reaction rate modeling coupled with crystal mineralogy and morphology analyses yield (i) quantification of PAsp's inhibition kinetics and capacity, (ii) substantial modulation of calcite crystal shape, and (iii) the latter to provide local templates for vaterite nucleation and growth, depending on the properties of the individual PAsp.

Formation and crystal structure of dolomite

16:30	16:50 (15 min speech+ 5 min discussion)	Georgina Lukoczki	Very high-magnesium calcite, protodolomite, and dolomite—What's the difference and how do we tell them apart?	The so-called 'Dolomite Problem' has puzzled researchers for a long time as to how exactly near-surface dolomites form and why there appears to be a secular variation in their abundance. Furthermore, a fundamental confusion remains about what exactly dolomite is and isn't. Very high-magnesium calcite, protodolomite, and dolomite are terms used, often incorrectly, to designate Ca-Mg carbonates of various Ca-Mg ratios and cation ordering. The issue of naming the minerals correctly is not only a concern of nomenclature but also carries important implications for the interpretation of geochemical data. This is especially true for samples that are mixtures of various Ca-Mg carbonate phases that are difficult, if not impossible, to physically and/or chemically separate. These issues will be explored using X-ray diffraction data on examples from various geological settings and ages, including modern lagoonal sediments from Brazil, Triassic dolomites from Hungary, and high-temperature dolomites from the American Midcontinent.
16:50	17:05 (10 min speech+ 5 min discussion)	Péter Pekker, Zsombor Molnár, Ferenc Kristály, István Dódon, Kornél Rácz, Ivett Pálfi, Enikő Magyar, Mihály Pósfai	STEM study of Ca-Mg ordering on atomic scale in protodolomite (experimental aspects and results)	TEM Z-contrast imaging is a useful tool for studying Ca-Mg ordering on the atomic scale in protodolomite; however, the experimental work can be challenging due to the sensitivity of protodolomite to electron-beam damage. With a carefully executed STEM data collection method we studied the relationship between the degree of Ca-Mg ordering (as obtained from the image contrast in high-resolution, high-angle annular dark-field images) and the local chemical composition (Ca/Mg ratio, as obtained using STEM EDS mapping) in protodolomite grains from the sediments of Lake Balaton. The results show an inhomogeneous structure and various Ca/Mg ratios within individual particles, with perfect dolomite-like ordering alternating with disordered Ca-Mg distribution in nm-scale domains.

Tuesday (05.07.2022)

Biogenic carbonates

9:00	9:25 (20 min speech+ 5 min discussion)	Laurence A. J. Garvie Zoom presentation	Life and the surprising carbonate diversity in the hot Sonoran Desert	<p>Vascular plants actively transport dissolved elements from the rhizosphere to above-ground plant structures. This conveyor-belt-like process plays significant roles in the biogeochemical cycles of elements such as Ca, Mg, Cl, and S, as certain plants concentrate large quantities of these elements in plant-hosted biominerals. For example, a single large columnar saguaro cactus (<i>Carnegiea gigantea</i>) contains on the order of 1×10^5 g of the Ca oxalate biomineral weddellite, with the Ca translocated from the soil into the plant by the roots and vascular system. However, the fate of these elements is dependent on the health of the plant and on the manner in which the plant dies. In this talk I illustrate the surprising diversity of carbonates associated with life in the Sonoran Desert including:</p> <p>A) The enclosed environment in decaying cacti, with the formation of decimeter-sized masses of monohydrocalcite $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ and nesquehonite $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, with localized lansfordite $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ and glushinskite $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.</p> <p>B) The diverse ash mineralogy following wildland fires, including the widespread formation of fairchildite $\text{K}_2\text{Ca}(\text{CO}_3)_2$, calcite, lime, and periclase from the paloverde tree (<i>Parkinsonia microphylla</i>), and formation of a new but common double carbonate "paulknauthite" sp. nov. $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ in the ash of the desert spoon (<i>Dasyliirion wheeleri</i>).</p> <p>C) The distinctive mineralogy associated with slime flux jelly on an infected tree (<i>Populus fremontii</i>) wound, with the formation of ikaite/monohydrocalcite/alpha sulfur in the jelly, which is surrounded by kalicinite KHCO_3, baylissite $\text{K}_2\text{Mg}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$, apthitalite $(\text{K},\text{Na})_3\text{Na}(\text{SO}_4)_2$, arcanite K_2SO_4, alpha sulfur, monohydrocalcite, calcite, aragonite, vaterite, weddellite, and nesquehonite.</p> <p>The common and widespread carbonate mineral diversity associated with vascular plants in the desert southwest of the USA, expands our understanding of bio-mediated mineralizing systems worldwide.</p>
9:25	9:45 (15 min speech+ 5 min discussion)	Nóra Tünde Lange-Enyedi	Microbially induced carbonate precipitation in cave environments	<p>Bacteria isolated from karst caves might induce the precipitation of different carbonates and their polymorphs, including amorphous calcium carbonate, calcite, magnesium calcite, aragonite, vaterite, and monohydrocalcite in laboratory experiments. Calcium carbonate deposition by bacterial species could be an important strategy for survival in high calcium cave environments. Numerous factors might affect the precipitation processes, including the environmental conditions, the bacterial extracellular polymeric substance, and metabolic characteristics. The aim of the talk is to discuss these phenomena.</p>

Formation and crystal structure of aragonite

9:45	10:05 (15 min speech+ 5 min discussion)	Marco Bruno, Mauro Prencipe, Dino Aquilano, Andrea Cotellucci, Stefano Ghignone, Péter Németh Zoom presentation	Calcite/aragonite epitaxy: a computational study for understanding shell formation in molluscs	<p>Understanding the selection mechanisms of CaCO_3 polymorphs (vaterite, aragonite and calcite) is pivotal for elucidating both inorganic and biogenic carbonate formation. It is peculiar that the same organisms originate different polymorphs and, what's more, these polymorphs can even be epitaxially related. Here we ask why some molluscs develop calcite (Cc) layers at the contact with aragonite (Ar) in the outer portion of their shell, while others do not. To establish the most likely epitaxial relationships between calcite and aragonite, here we investigated at empirical level (and OK) the $(001)\text{Ar}/(00.1)\text{Cc}$, $(110)\text{Ar}/(10.0)\text{Cc}$, $(010)\text{Ar}/(01.2)\text{Cc}$ and $(100)\text{Ar}/(11.0)\text{Cc}$ interfaces. By analysing the $(001)\text{Ar}/(00.1)\text{Cc}$ epitaxial and relaxed interface, we found that a hexagonal (space group, $P6322$) CaCO_3 polymorph is generated, corresponding to the phase recently identified by a molecular dynamic study on the high-temperature ($\sim 600\text{K}$) aragonite-calcite transition. This polymorph shows a symmetry intermediate between those of aragonite (orthorhombic) and calcite (rhombohedral), develops as a nanometric phase, and exhaustively explains the observed epitaxy, $(001)\text{Ar}/(00.1)\text{Cc}$. We propose that the growth of calcite at room pressure and temperature in the outer portion of the shell of molluscs is strictly associated with the formation of this hexagonal CaCO_3 polymorph. Moreover, we can envisage the findings have implications for understanding the sluggish mechanisms of aragonite-calcite transformation at ambient conditions.</p>
------	---	--	--	--

10:05	10:25 (15 min speech+ 5 min discussion)	Pavel N. Gavryushkin Zoom presentation	High-pressure and high-temperature polymorphism of calcium carbonate	Due to the active role of CaCO ₃ in the global carbon cycle, its high-pressure-temperature polymorphism attracted close attention of researchers and has been investigated for over 100 years. Despite this, new stable and metastable polymorphs are still discovered. In the presentation, we will show the results of theoretical and experimental investigation of calcite evolution on its compression up to the pressure of 1 Mbar and heating up to 2500 K, as well as identify the open questions of the CaCO ₃ P-T phase diagram.
10:25	10:45 (15 min speech+ 5 min discussion)	Aleksander Rečnik, Pavel N. Gavryushkin, Vesna Ribić, Péter Németh, Mihály Pósfai Zoom presentation	Monoclinic deformation of aragonite and formation of twin-based polytypes	Németh et al. (2018) recently reported the existence of monoclinic aragonite mAra, a new polymorph that was identified as a constituent of the first precipitate in cave drip waters, the formation of which precedes the crystallization of aragonite. We constructed series of aragonite supercells with different degrees of monoclinic deformation along the [11-0] axis and relaxed them by means of DFT optimization. Interestingly, depending on the degree of the monoclinic deformation, the supercells relaxed into new polytypic superstructures that resemble polysynthetic twins of aragonite. By this, we have potentially identified the mechanism of aragonite twinning.
10:45	10:55 (5 min speech+ 5 min discussion)	Vesna Ribić, Zsombor Molnár, Mihály Pósfai, Pavel N. Gavryushkin, Péter Németh, Aleksander Rečnik Zoom presentation	Discussion on the Hiragi–Makovicky reflections in aragonite	The first mention of this unusual diffraction condition was made by Hiragi et al. (1966) who observed superstructure reflections with half-integer indices, i.e. [$\frac{1}{2}$ 0], etc. in aragonite precipitated from CaCl ₂ and (NH ₄) ₂ CO ₃ solutions. As these reflections do not belong to the Pnma space group of aragonite, the authors explained them as a new Pcab polytype that is based on repeated [110] twinning of aragonite. Unaware of Hiragi's work, Makovicky (2012) described a new hypothetical polytype that would be a consequence of multiple twinning in every (110) layer. While [$\frac{1}{2}$ 0] reflections are commonly observed in aragonite, Pcab polytype has never been confirmed to exist. We provide an evidence that when a [110] twin of aragonite is observed along the [110] projection, [$\frac{1}{2}$ 0] condition is generated, imitating the Pcab polytype. By this, we identified a possible origin of the mysterious reflection condition in aragonite.
10:55	11:15	coffee break		
Lake and cave carbonates				
11:15	11:35 (15 min speech+ 5 min discussion)	Zsombor Molnár	The effect of smectite on the formation of CaCO ₃ minerals	Previous studies suggested that the presence of smectite nanoparticles strongly enhances the formation of calcite instead of other forms of CaCO ₃ . In laboratory experiments we synthesized CaCO ₃ both in the presence and absence of smectite, and studied the heterogeneous nucleation of calcite with various transmission electron microscopy techniques.
11:35	11:55 (15 min speech+ 5 min discussion)	Mihály Pósfai, Zsombor Molnár, Kornél Rácz, Péter Pekker, Vera Istvánovics	Precipitation and transformation of carbonate minerals in Lake Balaton	As the largest water body in landlocked Hungary, Lake Balaton has great economic, touristic and cultural significance. Concerns about silting and eutrophication-related water quality deterioration directed attention to the sediment, about 2/3 of which consists of carbonates that precipitated from lakewater. We focus on some recently discovered features of carbonate precipitation, including the roles of both algae and clay minerals in the nucleation of carbonates, the sequence of phase changes (from ACC through aragonite to calcite) that likely occur in the lake, and the special conditions that lead to the formation of Mg-rich carbonates (such as protodolomite). Another line of research aims at obtaining a better understanding of the roles of carbonate and other sediment minerals in phosphorus mobilization; we map the distribution of „visible P” (e.g., observable using STEM-EDS) in association with sediment minerals and identify the mineralogical phases of P-rich particles.

11:55 (10 min speech+ 5 min discussion)	12:10	György Czuppon , Attila Demény, Szabolcs Leél- Őssy, József Stieber, Mihály Óvári, Péter Dobossy, Ágnes Berentés, Richard Kovács	Carbonates formed in cave environments in Hungary	Carbonate deposits (e.g., stalagmites, flowstones) formed in caves are one of the most important climate archives from continental areas. In order to utilize the stable isotope ratios, trace element compositions, and petrographic characteristics of cave carbonates, it is necessary to determine the complex interaction and relationship between climate parameters and the response within the cave. Therefore, we investigated the isotopic and chemical compositions of recently forming carbonates in Baradla-, Béke caves in Aggtelek Karst, and in Ariadne-Ajándék cave system in Pilis Mt., and constrained the factors that influenced during their formation as well as determined the most suitable places for speleothem sampling.
12:30	13:30	Lunch break		
13:30	14:30	Discussion + closing		
14:30	15:45	Free time		
16:00		Bus travel to Balatonfüred from Veszprém Óváros tér		~16:30 arrival to Tagore promenade (short sightseeing), tour guided by Mihály Pósfai. 17:45 departure 18:00 arrival to Figula restaurant 18:00-21:30: wine sampling and workshop dinner 21:30: departure 22:00 arrival at Óváros tér

Wednesday (06.07.2022)

Departure or excursion to Csodabogyós cave (departure 09:00), tour guided by György Czuppon