RECENT ARAGONITE FORMING IN DRIPPING MINERAL SPRINGS FROM CORUND, ROMANIA

Zoltan Pal[1], Tudor Tamas[2], Lucian Barbu-Tudoran[2], SimonaCinta-Panzaru[3]
[1] Babes-Bolyai University Cluj Napoca, Doctoral School of Physics
[2] Babes-Bolyai University Cluj Napoca, Department of Geology
[3] Babes-Bolyai University Cluj Napoca, Biomolecular Physics Department
palzeusz@gmail.com

Abstract

Keywords: $CaCO_3$ polymorphs; Recent carbonate deposits; Raman Spectroscopy
Domain: physics
Section: Elaboration of the doctoral thesis

Motivation
New research is conducted on the recent and old deposits of carbonates of Corund area, where former aragonite and calcite mining and grinding/polishing activity was established 110 year ago. Coexistence of calcite and aragonite polymorphs in naturally occurring carbonate rocks of Corund, Romania was subject of few controversial, early studies, yet uncompleted according to the current standards [1],[2]. This paper is organic part of the doctoral thesis conducted under the supervision of PhD School of Physics in Babes-Bolyai University, Cluj Napoca.

Methodology of Research
This paper describes calcium carbonate horizons formed in dripping convex surface of travertine fed by a highly mineral spring in Corund, Romania, relying on multi-laser micro-Raman spectroscopy, X-ray diffraction and optical microscopy. A 3-month period of dripping surface depositions are gathered on 6 glass slides placed under the continuously dripping water channels. A 25 mm cross-section of a recent stalagmite is analyzed with Raman spectroscopy.
In the broader doctoral Thesis, we also use XRD and Scanning Electron Microscope, UV-VIS and chemical analysis for water samples, FT-Raman for evaporites.

Results and Comparison with State-of-the-art
Similar structures have been described occurring at the surface. [3]. An overview of the spring travertine is shown in Fig. 1., The slides were placed either under drape-like stalactites, or in micro pools filled with dropping water. 3 of the 6 slides have greyish colored deposits, the other 3 have crusts of probably Iron hydroxides due to changing occurred in mineral composition of the spring water during this 3-month period – see the Fig 1. with evident reddish diffuse flow channels.
The morphology and building minerals of thin layers on the slides are discussed. Raman spectra collected in the 785 nm line excitation revealed the presence of Aragonite, Calcite, Gypsum, Quartz (due to surface flush of fine sand deposits around the spring). Weakly developed aragonite crystals build up the base matrix of the thin carbonate layer developed on both sides of the slides.
XRD measurements, EMS imaging and water analytics are further used to discuss and build up the deposition model of aragonites in normal surface condition, despite their thermodynamically metastability. These results are discussed considering other author's similar results [4] regarding the biogenic carbonates in stromatolites. Due to the Mg/Ca ratio and the alkalinity of the drip-ping water, the comparison with proto-Aragonite and monoclinic-Aragonite [5] - as precursor stages of the metastable aragonites - is discussed.

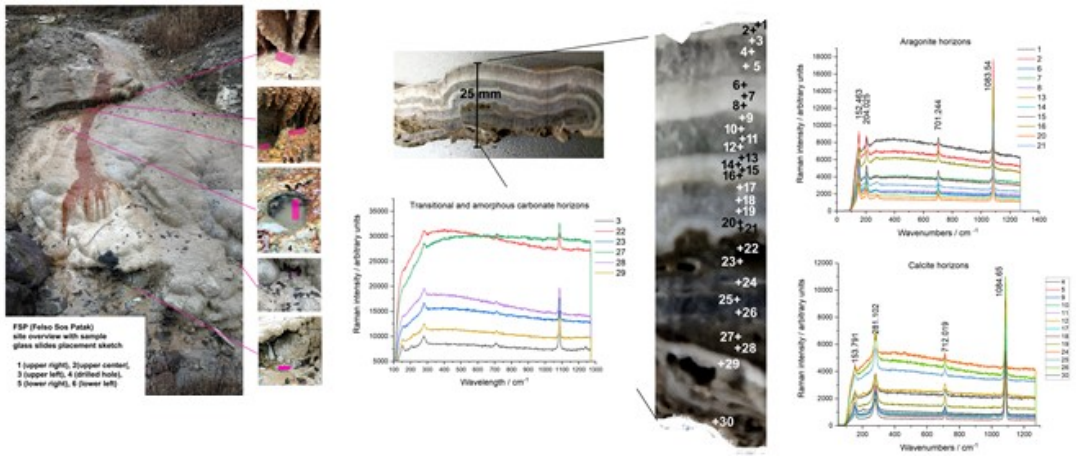

Figure 1: a: the bird-eye view of the carbonate bank deposited by the spring near Felső Sós Patak (Upper Salty creek) and the position of the glass slides during the 3-month period between 12.12.2019 and 11.03.2020. Corund, Romania. b: cross section Raman measurements through a stalagmite formed in the 6 (Lower left) position revealed a systematic alternance of Aragonite and Calcite horizons.

Conclusions

Recently deposited carbonates show the alternating structure of Calcite-Aragonite layers in normal, surface conditions. The thickness of the alternating layers is similar, showing that the overall condition changing period has to be similar. Probably is related with the cold/warm half year alternation.

The recent dripping depositions on the lower side of the glasses shows the carbonate crystallization induced on the surface of the CO_2 bubbles, having a much clearer vibrational response compared with the above mentioned proto- or monoclinic Aragonite.

Acknowledgements

I would like to express my very great appreciation to Ptof. Dr Simona Cinta-Panzaru for her valuable and constructive suggestions during the planning and development of this research work. I would also like to thank Dr. Tudor Tamas, for his advice and field work assistance in keeping my progress on schedule. I would also like to extend my thanks to the technicians of the laboratory of the Physics and Geology departments, and for their help in offering me the resources in running the program.

References

[1] Nicolae Metta: Cateva observatiuni la analiza unui exemplar negru de carbonat de Calciu de la Korond (Ardeal), In: Dari de seama ale sedintelor Institutului geologic al Romaniei. 1930, XVI 1927-1928, pp. 36-40.

[2] Sandor Koch: A lévai (Levice, Csehszlovákia) és a korondi (Corund, Románia) forráskövek, In: Acta Mineralogica, Petrographica. Institutum Mineralogicum et petrographicum Universitatis Szegediensis 1949, p. 17-29.

[3] Jennifer A. Barth, Henry S. Chafetz: Cool water geyser travertine: Crystal Geyser, Utah, USA, In: Sedimentology, Vol 62 Issue 3, 2015. pp. 1-14, DOI: 10.1111/sed.12158

[4] Karim Benzerara, Anders Meibom, Quentin Gautieri, Jozef Kazmierczak, Jaroslaw Stolarski, Nicholas Menguyi, Gordon Brown, Nanotextures of Aragonite in Stromatolites from the Quasi-Marine Satonda Crater Lake, Indonesia, Geological Society London Special Publications 336(1) pp.211-224, 2010 DOI: 10.1144/SP336.10

[5] Péter Németh, Enrico Mugnaioli, Mauro Gemmi, György Czuppon, Attila Demény, Christoph Spötl, A nanocrystalline monoclinic $CaCO_3$ precursor of metastable aragonite, Science Advances, Vol. 4 (12), 2018 DOI:10.1126/sciadv.aau6178