# EXPERIMENTAL STUDY OF THERMAL WATER RELATED HYDROCHEMICAL AND PRECIPITATION PROCESSES

THESES OF PHD DISSERTATION

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2020

## 1. Introduction and objectives

The active hypogene karst area of Buda Thermal Karst, situated in the regional discharge zone of a thick carbonate range, is a natural laboratory where ongoing dissolution and precipitation processes can be studied. Thermal waters with high total dissolved solid and $CO_2$ content and with low dissolved oxygen concentration arise to the surface. Discharging thermal springs can be found in small spring caves. Because of intensive thermal water production for balneological purposes, the volume discharge of springs has significantly decreased, resulting in an almost stagnant condition in the thermal spring pools. The detailed investigation of the area's hydrogeological situation and thermal water composition gave the background of the analysis of complex discharge phenomena. Based on the study of biogeochemical precipitates (biofilm) and calcite rafts, forming in spring caves, a conceptual model was proposed about the processes behind these phenomena [ERŐSS, 2010].

As *in situ* measurements could only indirectly prove the processes, the main goal of my study was to design and perform an *in situ* experiment to demonstrate these mechanisms. In the experiment, the physicochemical parameters of the flowing thermal water and the related forming precipitates were analysed simultaneously excluding dissolution processes. Taking into account the previously known properties of the spring waters and related precipitates of the Buda Thermal Karst, the following were studied during the *in situ* experiment: characteristics of the precipitates, their relationship with the physicochemical parameters of the thermal water, the reason for their formation, their development over time and along the flow path, the effect of the forming precipitates on the thermal water, the adsorption capacity of the biogeochemical precipitates, the temporal evolution of the amount of adsorbed elements (trace elements and radionuclides), especially the amount of adsorbed $^{226}Ra$ and its effect on the $^{222}Rn$ activity concentration of the water.

## 2. Applied methods

During the *in situ* experiment, different water and air parameters were measured, and the biogeochemical precipitates were analysed with different methods.

The field parameters of the **thermal water** (temperature, pH, specific electrical conductivity, dissolved oxygen content) were measured on site with an HQ40d Multi-Parameter Meter. Water temperature and specific electrical conductivity were recorded by CTD Diver, pH was recorded by a Greisinger GMH 5550 device equipped with a Greisinger GE 100 BNC pH electrode. The concentration of major ions ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $HCO_3^{-}$, $Cl^{-}$, $SO_4^{2-}$) were determined by conventional laboratory techniques (titration, flame photometry, turbidimetry, Department of Microbiology, Department of Geology and Department of Physical Geography, Eötvös Loránd University). The activity concentrations of $^{226}Ra$ and $^{234}U$+$^{238}U$ were measured by alpha spectrometry (Imre Müller and Heinz Surbeck Hydrogeological Laboratory, Department of Geology, Eötvös Loránd University). The activity concentration of $^{222}Rn$ was measured by liquid scintillation method on a Tricarb 1000TR instrument (Department of Atomic Physics, Eötvös Loránd University). The concentration of trace elements was analysed by mass spectrometry (ICP-MS Element 2, Thermofinnigan, Department of Analytical Chemistry, Eötvös Loránd University). The $\delta^{18}O$, $\delta D$, $\delta^{13}C$, $\delta^{34}S$ stable isotope composition of the water was measured with a Thermo Finnigan Delta plus XP stable isotope ratio mass spectrometer (Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Hungarian Academy of Sciences). The sulphide concentration was examined with a UV / VIS Evolution300 instrument (EPA Method 376.2: 1978, MSZ 448-14: 1990), while the methane concentration was examined with an HP-5890-GC_01-FID / TCD instrument (WBSE-27: 2002) (Wessling Hungary Kft. ). In addition to the measurement of the above water physicochemical parameters, the partial pressure of $CO_2$ and the saturation

index with respect to calcite were calculated with PHREEQC-2 hydrochemical modeling software. A reactive transport model was also performed with the PHREEQC-2 software to demonstrate the physicochemical processes along the water flow. The relationship between the individual measured and between the measured and modelled parameters was examined by correlation analysis using SPSS software. **Air** temperature and relative humidity were measured with a Voltcraft DL-120TH instrument.

The temporal development of **biogeochemical precipitates** formed from thermal water was investigated with an Olympus BH2 type (Department of Geology, Eötvös Loránd University) and a light microscope (Department of Microbiology, Eötvös Loránd University). The mass of the precipitates was measured with a Mettler Toledo B154 analytical balance (Department of Geology, Eötvös Loránd University). After lyophilization of the precipitates, the following methods were used to determine the mineral and elemental composition, iron phases, radioactivity and stable isotope composition: X-ray powder diffraction (Siemens D5000 X-ray powder diffractometer, Department of Mineralogy, Eötvös Loránd University), mass spectrometer (Department of Analytical Chemistry), Mössbauer spectroscopy (WISSEL and KFKI Mössbauer spectrometers, Department of Analytical Chemistry, Eötvös Loránd University), gamma spectroscopy (Canberra-Packard BE5030-7915-30ULB gamma spectrometer, Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Hungarian Academy of Sciences) and Thermo Finnigan Delta plus XP stable isotope ratio mass spectrometer (Isotope Climatology and Environmental Research Centre, Institute for Nuclear Research, Hungarian Academy of Sciences). The structure and morphology of the precipitates were examined with an EVO MA 10 Zeiss scanning electron microscope (Ecological Research Center, Hungarian Academy of Sciences), and an AMRAY 1830 scanning electron microscope (Department of Petrology and Geochemistry, Eötvös Loránd University).

## 3. Results, theses of the dissertation

The main goal of my doctoral research was to study the formation of thermal water related precipitates and the determining processes in the discharging thermal waters of the active hypogene karst system of the Buda Thermal Karst. For this purpose, I designed and performed an *in situ* experiment in which the physicochemical parameters of the thermal water and the related precipitates were investigated simultaneously along the flow path of the thermal water.

Based on measurements of different water and air parameters, analysis of precipitates and reactive transport modeling, the main results of the *in situ* experiment can be summarized in the following theses:

1. I was the first to develop and perform a systematic *in situ* experiment in the Buda Thermal Karst and also internationally. The experiment simulated the discharge of thermal springs of a hypogene karst system and the processes after the discharge under controlled conditions. During the experiment, by monitoring and modeling the discharge and flow of the thermal water, I simultaneously monitored the characteristics and changes of the water and the related precipitates, excluding the dissolution processes. The preparation, conditions, and results of the *in situ* experiment form the basis for conducting similar experiments in other areas and for investigating further parameters.

2. I found that the temperature, pH, dissolved oxygen content and specific electrical conductivity of the thermal water wells of the Gellért Hill area are constant over time based on the three-month monitoring, in accordance with the previous, but only occasional field measurement results. With this, I have shown that in the *in situ* experiment, the temporal changes in the field parameters of the discharging thermal water do not have to be taken into account when interpreting the changes along the water flow.

3. With the monitoring of the physicochemical parameters along the water flow and with reactive transport modeling, I confirmed the previously

assumed processes in the thermal spring caves of the Gellért Hill discharge area [ERŐSS, 2010]: the degassing of dissolved $CO_2$ and $^{222}Rn$ from the water and the dissolution of atmospheric oxygen. The relationship of each parameter was also confirmed by correlation analysis. Based on my research, I have shown that the parameters of cave air have no effect on the processes taking place in the water.

4. I proved that the microbiological and physicochemical processes at the discharge are not sharply separated from each other, they take place simultaneously. So, the term biogeochemical precipitate, introduced by [DOBOSY et al., 2016], can be applied. However, in the dominant character of the forming precipitates, I showed a longitudinal and temporal sequence. I identified two subtypes of the forming biogeochemical precipitates and accordingly introduced the following new nomenclature: 1) "biofilm-like biogeochemical precipitate" and 2) "carbonate-like biogeochemical precipitate". I propose to use the new terminology as follows, which I also follow in my dissertation:

- "biofilm-like biogeochemical precipitate", in short "biofilm", in which the presence of microorganisms and microbiological processes (e.g. the production of extracellular polymeric substances (EPS)) dominate and contains few mineral particles,
- "carbonate-like biogeochemical precipitate", in short "carbonate", in which physicochemical processes are dominant, therefore the crystalline phase of $CaCO_3$ dominates, where cell clusters formed by microorganisms can be observed on the surface of the crystals or in the crystals.

5. The discharging reductive thermal water with low dissolved oxygen content becomes oxidative due to the dissolution of atmospheric oxygen, so the dissolved $Fe^{2+}$ is oxidized. As a result, a ferrihydrite-containing biofilm is formed close to the discharge, at the first 8 m. Based on the comparison of the modeling and measurement results, I suppose that the process of ferrolysis

may inhibit carbonate formation where ferrihydrite is formed.

6. Comparing the results of the performed *in situ* flowing thermal water experiment with the stagnant thermal water experiment [BURKUS, 2017; ANDA, 2019], I demonstrated that the formation of mature biofilm, the rate of biofilm formation and the amount of elements adsorbed by the biofilm correlate with the water hydrodynamics. The continuously flowing thermal water promotes biofilm formation by constantly transporting planktonic microorganisms to the precipitation surface, as well as various nutrients and energy sources necessary for their growth and reproduction.

7. With my research I showed that the large amount of adsorbed $^{226}$Ra (8000–10000 Bq/kg) causes an increase in the dissolved $^{222}$Rn activity concentration (by 130 Bq/l) even in a short time (in a few weeks under the experimental conditions). I was the first to prove the intensive degassing of dissolved $^{222}$Rn in the Buda Thermal Karst by measurements and reactive transport modeling. I also detected the presence of $^{210}$Pb, the daughter element of $^{222}$Rn, and found that it is incorporated into the carbonates formed along the water flow in the proportion of dissolved $^{222}$Rn, thus following its decrease along the flow.

8. By simultaneously examining the thermal water and the carbonate forming from it, I could give the critical supersaturation value for carbonate precipitation from the discharging thermal waters of the Gellért Hill area. The precipitation of carbonates starts at 5–10 supersaturation values. This can be a reference value, because here the carbonate has been proven to formed from the water it assorts with. This is often questionable in the case of precipitates of natural spring systems.

9. By examining the development of biogeochemical precipitates, I discovered that the boundary of biofilm and carbonate formation changed not only in space but also over time during the experiment. By simultaneously measuring the physicochemical parameters of the water, I proved that the

increasing $CO_2$ degassing over time pushed the location of the critical supersaturation value for carbonate closer to the discharge (by 30–40 m under the conditions of the 12-week-long experiment). As a result, the boundary of carbonate precipitation also became closer to the discharge. For this reason, there was a section in the experiment where first biofilm and then carbonate were formed. This transition was also followed by the concentration of some trace elements (Al, As, Fe, Pb).

10. I determined that the carbonate precipitation rate under the conditions of the *in situ* experiment was 0,34–2,66 g/cm$^2$/year. However, I have shown that its values vary over time, along the water flow, and locally. With the detailed documentation of the experimental conditions and the physicochemical parameters of the water, the precipitation rate values also serve as a reference and comparison basis for the evaluation of the results of other carbonate formation systems.

11. I distinguished two types of the forming carbonates based on the crystal morphology: 1) carbonate with independent rhombohedral crystals and crystal groups, formed under relatively low supersaturation conditions and influenced by microbiological processes, 2) spear-shaped complex crystal aggregates formed by rhombohedral crystals, which were previously found in the calcite rafts of the active spring caves in Gellért Hill [VIRÁG et al., 2013; AMBRUS, 2014; VIRÁG, 2018]. Its formation is caused by rapid $CO_2$ degassing and high (13–17) carbonate supersaturation level.

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