COMPLEX GEOCHEMICAL, PALEOCLIMATOLOGICAL AND TECTONIC INVESTIGATIONS ON CONTINENTAL CARBONATE DEPOSITS IN HUNGARY

FINAL REPORT

Introduction

The main themes of the project were: 1) investigations on Hungarian travertine and tufa occurrences, 2) analysis of recent carbonate precipitation from thermal waters and 3) studies on cave-hosted tufa dam formations and their comparison with speleothems along with site monitoring. During the investigations the original goals slightly changed. Many travertine and tufa occurrences turned out to be highly contaminated with detrital Th that made their U-series dating impossible. Those cave-hosted tufa occurrences that were drilled and seemed to be appropriate for further analyses yielded mainly young (<4000 years) ages with rarely precise U-series ages. Several papers were published in the literature during the project period that forced us to change the studies in order to obtain results that may reach a better impact and provide the basis of publications in leading journals. Hence new methods were used (e.g., radiocarbon dating of cave-hosted tufa occurrences, and clumped isotope analyses of travertines), new occurrences were included (e.g., to reach a wider temperature range for the recently forming carbonate analysis), and new aspects were studied in details (e.g., extended cave monitoring including analysis of freshly precipitated carbonate at several sites, or investigation of old speleothems in order to expand the time range covered). Hence, although the main goals were followed, the research subjects were focused on scientific problems that we encountered during the project's implementation. In this way we managed to publish most of the results in leading journals of the geochemistry and paleoclimate fields (Geochimica et Cosmochimica Acta, Hydrological Sciences Journal, International Journal of Speleology, Quaternary Science Reviews, Scientific Reports). Due to theme focusing, the planned structural geological analyses were only partly conducted. It was realized that another „OTKA" project was also conducted in this period dealing with incision rates and comparison of travertine ages and cosmogenic isotope ages. With the participation of the researchers of the two projects a poster was presented at the European Geosciences Union conference in 2016, hence in the present project the theme was not elaborated further.

In the following the main results are described for the three main themes, the names of principal investigators of the individual themes are also given.

Investigations on travertine and tufa occurrences (Sándor Kele)

Pleistocene travertines from the Gerecse and Buda Hills

The most important travertine bodies of the Gerecse and Buda Hills were visited and sampled in order to choose sections for detailed studies. The original work plan had involved detailed sampling of several travertine sites from the Buda Hills (e.g. Budakalász, Felső Hill, Kálvária Hill), but these travertines were not useful for high-resolution radiometric dating due to their high Th-contamination. Results from the sedimentological, geochemical and reservoir geological study of the Budakalász travertine were published in Quaternary International (Claes et al., 2016).

Based on field trips in the Gerecse Hills and former radiometric age data (Kele, 2009), we chose the travertine of Süttő and Dunaalmás quarries for detailed analyses. The most suitable samples for U-series dating were the travertines of the Süttő Új-Haraszti and Hegyháti-quarry, thus, we decided to continue with detailed sampling at these places. The Új-Haraszti quarry was sampled in detail along a vertical section using a drilling device. 14 samples were selected for U-series dating at the laboratory of NTU (Taipei, Taiwan). Based on the results the studied travertine body was deposited during the Middle-Pleistocene, between 415 and 148 ky. Sedimentological, structural geological and reservoir geological study of the travertine of Süttő, Gazda-quarry was performed in relationship with a Belgian-Hungarian TraRAS reservoir geological project (Török et al., 2016). The Sugar Quarry of Süttő was sampled in detail as well. Fissure ridge like structures were also observed, interpreted as the main discharge points of the paleosprings in the area that could have played the major role in the deposition of the travertines of Süttő. Stable isotope analyses have been conducted, radiometric dating and structural analyses are still in progress. The Vértesszőlős travertine was also selected for further studies considering its significance due to the presence of Early man remnants. Dating of Vértesszőlős travertine was also performed at NTU (Taipei, Taiwan) and provided age data between 350-300 ky. Results of clumped isotope analyses of the Vértesszőlős travertine were presented at international conferences: the 5th International Clumped Isotope Workshop, St. Petersburg, Florida, USA (Kele et al., 2016a) and the 5th Geological-Palaeontological-Archaeological Discussion 2016, Ganovce, Slovakia (Kele et al., 2016b). Publications of the data are in progress.

Clumped isotope analyses of recently forming carbonates and travertines

The travertine theme was extended with clumped isotope analyses facilitated by a SCIEX postdoctoral scholarship (ClumpIT; Nr: 13.071-2) provided to Sándor Kele at the ETH, Zürich. Most of the analyses was focussed on the calibration of the clumped isotope thermometer and the calcite-water oxygen isotope thermometer based on recent travertine and tufa samples, in accordance with the work plan of the OTKA project. The main advantage of the recently developed clumped isotope technique is the proportionality between the deposition temperature of carbonates and their clumped isotope (Δ_{47}) values, while the method requires no assumptions on the oxygen isotopic composition of the carbonate precipitating solution. The previously published, Δ_{47}-based calibrations are based mainly on

carbonates precipitated in the laboratory, on biogenic carbonates and on theoretical considerations, covering a limited temperature range. In this study stable- and clumped isotope compositions of 51 recent travertine and tufa samples composed of calcite, aragonite and their mixtures were determined. The studied samples were formed in the 5-95 ^{o}C temperature range, mainly around thermal springs and wells both in Hungary (e.g. Egerszalók, Igal, Széchenyi Spa) and abroad (e.g. Pamukkale, Turkey; Yellowstone, USA; Italy, etc.). The travertine-based empirical Δ_{47} –T travertine calibration curve can be used for different type of carbonates and in several research areas including paleoclimatology and reservoir geology and it is used now as the calibration of the method applied at ETH for clumped isotope analyses. The results of the calibration of the clumped isotope thermometer and the calcite-water oxygen isotope thermometer were published in the leading geochemical journal *Geochimica et Cosmochimica Acta* (Kele et al., 2015) and they were presented at international conferences (pl. Goldschmidt, Sacramento, USA; IAS, Geneva, Switzerland), and as invited talks. Additional papers are in preparation based on the results obtained during clumped isotope analyses of further occurrences (e.g. Süttő, Vértesszőlős).

Freshwater tufa deposits

Tufa deposits of the Sebesvíz Valley (Bükk) were sampled using a drilling device, but the samples were poor quality and friable. There was no observable lamination within the drilling cores and the carbonate was contaminated with detrital Th, so the detailed geochemical study of this surface tufa deposits in the Sebesvíz völgy were stopped. However, some stable isotope analyses were performed on both the tufa and water samples. The tufa dams and karst water of the Szalajka Valley were studied along the valley, in order to represent downstream changes and the effect of kinetic isotope fractionation in different seasons. In situ field measurements of physicochemical parameters and stable isotope, clumped isotope and trace element analyses were performed on the samples. The study of the tufa deposits at the Szalajka spring section was published in Karsztfejlődés (Bódai et al., 2016).

Study on the factors governing carbonate-water oxygen isotope fractionation (József Deák)

In order to refine the temperature dependence of carbonate-water oxygen isotope fractionation we studied a set of recently forming carbonate deposits (travertines, scales and speleothems) from Hungary. The currently available fractionation equations are based on the assumption that the temperature of depositing water is the only factor controlling the oxygen isotope fractionation between water and the deposited carbonate. The oxygen isotope and water temperature data measured in this study and complemented with archive Hungarian data yielded a well defined relationship. Additionally, the recently forming carbonate samples showed a pH-dependence, providing a pH correction equation that can significantly reduce the uncertainty of the empirical fractionation equation. Similar pH dependence was detected for published data, too, which supports our observation. Using

these results a new correction equation was established for published and widely applied fractionation relationships. The correction procedure would significantly decrease the mean and the standard deviation of offsets, improving the reliability of the paleotemperature calculations. A manuscript was prepared on the basis of the results that is just to be submitted to the journal *Isotopes in Environmental and Health Studies*.

Cave monitoring (György Czuppon)

In order to better understand the caves' operation and the transfer functions between environmental parameters and geochemical data, systematic monitoring was conducted between January, 2013 and July, 2015, followed by occasional collection and measurement activity until April, 2016, in the Béke and the Baradla Caves. Four sites (Nagy-tufa, Felfedező-ág, site of B560, Buzogány-Hall) within the Béke Cave were visited every month, while one site (Nehéz-út) in the Baradla Cave was visited occasionally especially in the first year of the monitoring campaign. The monitoring activity within the cave system included measurements of climatological parameters (temperature, relative humidity, pressure, cave air pCO_2), drip rate and collection of water samples for different parameters. Different "types" of water were collected within the caves: 1) drip water collected for approximately a month; 2) fresh drip water collected during visits; 3) stream water; and 4) spring water at the Nagy-tufa. Additionally, calcite farming was conducted by putting light bulbs (with a form analogous to stalagmite top) under active drip sites in the Buzogány Hall, Béke Cave for several months to allow deposition of carbonate in sufficient amount and were replaced four times.

The stable isotope composition of drip waters and the temperature at each site studied in both caves showed constant values with no significant variability (no seasonality) during the entire monitoring campaign, indicating a well-mixed aquifer with a relatively long residence time in the karst. The isotopic composition of the drip water was more negative than the amount weighted annual precipitation value, indicating more contribution from winter precipitation. CO_2 concentration showed strong seasonality (high values in summer and low values in winter) in both caves likely affecting carbonate precipitation or corrosion and consequently stalagmite growth. Systematic variations among Mg/Ca and Sr/Ca, Na/Ca, and Si/Ca element ratios have been detected in the drip water, suggesting Prior Calcite Precipitation (PCP). Freshly precipitated carbonate samples were also studied by means of stable isotope, trace element and radiocarbon analyses. A manuscript presenting these results has been accepted for publication by the International Journal of Speleology.

In order to have more comprehensive picture of the stable isotope composition and the origin of precipitation which strongly determine the composition of infiltrating water (hence drip water); precipitation samples have been collected at several locations. Using sector analysis of 4-days backward trajectories together with the calculation of evaporation and precipitation fluxes based on the specific humidity, as well as stable isotope data, contributions of different moisture sources were diagnosed, namely Mediterranean, Atlantic

region, northern Europe, eastern Europe, and local moisture. The results suggest that the stable isotope composition of precipitation preserved information regarding to the origin of the water vapor. A manuscript presenting these results has been accepted for publication by the Hydrological Sciences Journal.

Speleothems as recorders of past temperature, humidity and precipitation seasonality (Attila Demény)

Studies on speleothems were conducted in four main directions. In the followings the main results of the four sub-themes are described.

Recently forming speleothems

Four actively forming stalagmites were collected in the Baradla Cave where a three-year monitoring campaign was also conducted. Fast and slowly growing stalagmites have different stable carbon and oxygen isotope compositions as well as trace element contents that could be attributed to differences in dripwater migration pathways. The stable isotope compositions were compared with meteorological data of the last ~100 years indicating that carbon isotope compositions of the stalagmites may reflect changes in precipitation amount, while oxygen isotope compositions are more related to temperature variations. A paper has been published in *Central European Geology* (Demény et al., 2017a).

The combined textural-geochemical-meteorological interpretation lead us to select the isotope record that can best reflect variations in environmental conditions and can be used for further evaluation of the climate-proxy relationships. Detailed statistical analyses including wavelet coherence analysis has also been conducted, a manuscript is being prepared for submission to the journal *Earth System Science Data*.

Fluid inclusion analyses have been conducted on some of the recently forming stalagmites and the flowstone called Nagy-tufa (Béke cave) using a newly developed method (established during an earlier project, OTKA CK 80661). A recrystallization-induced O isotope shift was observed due to recrystallization of speleothem carbonate, indicating that the O isotope compositions of inclusion-hosted water may not be used for paleoclimatic or paleohydrological evaluation, whereas the H isotope compositions can preserve the original climate information. The results have been published (Demény et al., 2016a Quat Int) and served as the base for a follow-up study.

Formation of amorphous phase in freshly precipitating carbonate

The earlier study (Demény et al., 2016a Quat Int) lead us to assume that formation amorphous calcium carbonate (ACC) may be responsible for the recrystallization and associated isotopic changes. Such metastable carbonate formation may have severe consequences on the speleothems' sensitivity to diagenetic alteration, hence the possibility

was studied in details. Using an innovative sampling protocol and a combined application of different methods (infrared spectroscopy, X-Ray diffraction, scanning and transmission electron microscopy, stable isotope mass spectrometry) formation of ACC was detected successfully and its isotope fractionation relative to calcite was determined. The results have been published in *Scientific Reports* that belong to the Nature journal family (Demény et al., 2016b SciRep).

Paleohumidity changes in the Holocene revealed by flowstone data

Flowstones formed from springs in the Baradla and Béke Caves were drilled at several locations. Non-systematic distribution of stable isotope and chemical compositions along sections on the surfaces of flowstone occurrences indicate irregular formation and the possibility of hiatuses within the flowstones' edifices. Approximately ~40 cm long drill cores were extracted from the Nagy-tufa flowstone (BNT-2 core) and the Havasok flowstone of the Baradla Cave. U-Th dating efforts resulted in very large age uncertainties for the BNT-2 core, owing to detrital Th contamination. Therefore, in addition to the U-Th dating, AMS radiocarbon analyses were conducted to establish reliable age-depth models. The raw 14C ages were corrected for the dead carbon fraction (dfc) using radiocarbon results obtained for samples that yielded also accurate U-Th ages. Calibration and age-depth modeling have been performed using the OxCal v4.2.4. software. The data prove that the flowstones in the studied caves were formed contemporarily, covering the last ~4 ka with two major hiatuses around 3.5 and 1 ka BP. Inclusion-hosted water contents, stable carbon and oxygen isotope compositions of carbonate, and hydrogen isotope composition of inclusion-hosted water as well as Si contents were determined for the two cores and compared with regional paleoclimate records for the period of 3.5 to 1 ka BP. The water contents, δ^{13}Ccarb values and Si contents show correspondence with paleoprecipitation proxies from Central Europe to western Anatolia, while the paleotemperature estimates obtained using the δDwater values were in agreement with temperature reconstructions derived from paleobiological proxies from nearby lake sediments. These correlations indicate that the flowstone data provide valuable information about the regional water balance fluctuations for the late Holocene. A manuscript is being prepared for submission, the results will be presented at the European Geosciences Union conference with the support of the Research Centre of Astronomy and Earth Sciences.

Climate change events during the last interglacial

During planning the research activity, it was assumed that the thick flowstone and tufa dam occurrences may cover a larger time period, but finally it turned out that those providing acceptable age data cover only the late Holocene. Based on the knowledge of cave operation and the new climate-composition relationship observations, we revisited a stalagmite whose preliminary data indicated ages covering the last interglacial in order to determine how the Baradla Cave's area behaved during a major climate change period. The age-depth relationship was determined using 16 new U-Th dates supplementing the earlier set of 7

dates. High-resolution C-O isotope data on the carbonate (>500 analyses) as well as fluid inclusion δD-δ^{18}O values provided a base for the paleoclimatic interpretation. A set of climate change events was recognized not only in the studied stalagmite, but also in other European speleothem records that lead to a spatial climate change pattern. The regional differences and climatic changes appeared to be related to the variations in the North Atlantic ocean currents. The results have been published in the leading journal in paleoclimate, the Quaternary Science Reviews (Demény et al., 2017b).

Summary

Although some of the aspects of the original research plan had to be slightly changed and the cave-hosted speleothems and the travertine occurrences could not be compared due to the very different age ranges, the project resulted in a set of results that solved several scientific questions, revealed hitherto unrecognized relationships and provided a good base for future studies. Cave monitoring produced valuable data that can be published alone in an international journal (Czuppon et al., 2017), but other studies had to wait until the monitoring results reached an appropriate time length. Then the monitoring data could be successfully used for the interpretation of geochemical proxy values and publications of such data became possible even in high-rank journals (Demény et al., 2016b; 2017b). A similar situation occurred with the study on thermal water related carbonate precipitations that revealed a pH dependence of O isotopic fractionation (Deák et al., 2017) that helped interpret some of the carbonate formation monitoring data of Czuppon et al. (2017). The thermal water related carbonate data were studied along with fossil travertines using the clumped isotope method that serve as calibration for future studies (Kele et al., 2015). The paleoclimate information gathered during the application studies contribute to the knowledge of the behavior of the Carpathian Basin during climate change processes and can be used in the evaluation of climate change scenarios.