KH-17 125584 final report

This NKFIH project entitled „**Reconstruction of paleotemperature based on stable- and clumped isotope geochemistry of freshwater carbonates**" started in September 2017 led by Sándor Kele, the Principal Investigator (PI). Originally, the project was planned for two years (from 01-09-2017 to 31-08-2019) but then extended with additional 6 months until 29-02-2020. The project was primarily based on the use of the stable and clumped isotope method, U–Th and C–14 dating methods and applied on several types of continental carbonates including travertines, tufa and soil carbonates. Due to the short lenght of the project and instrumentational difficulties with the clumped isotope analyses, however, some analyses and related manuscripts could not be finished within the project, but they were partly presented at conferences and are being prepared for publication. To conclude, the project was spent in accordance with the project plan and the original plans have been completed by other studies, mostly on foreign tufa and travertine deposits (e.g. Egyptian tufa deposits, Italaian and Turkish calcite veins and fissure ridges, mollusk shells, dolomites). Thus, the project evolved to include several research directions with the leading role or active participation of the PI. Altogether 7 papers were published in Q1 journals with the financial support of NKFIH, other 3 papers (2 of them Q1) are in submission or under review and other 5 papers are in preparation. The main achievements (the not published ones more in detail) are presented separately below:

1) New data for the "Sahara Greening Periods" from the Western Desert: the tufa carbonates of the Kurkur-Dungul area (Southern Egypt);
2) Paleotemperature reconstruction of Pleistocene travertines from the Gerecse and Buda Hills;
3) Microfacies- and diagenesis study and U-Th dating of the Süttő travertine complex;
4) Fracture-filling calcites of the Pleistocene Süttő travertines;
5) Study of fault-related veins from Italy and Turkey;
6) Paleotemperature study of soil carbonates from Hungary;
7) Study of freshwater tufa deposits from Hungary;
8) Study of travertine and tufa from Slovakia and Romania;
9) Universal clumped isotope calibration efforts;
10) Factors controlling clumped isotopes and $\delta^{18}O$ values of hydrothermal vent calcites;
11) Clumped isotope temperatures from dolomites.

1.) New data for the "Sahara Greening Periods" from the Western Desert: the tufa carbonates of the Kurkur-Dungul area (Southern Egypt) (Sándor Kele)

The presence of travertine and tufa deposits in the driest areas on Earth has high importance in palaeoclimate reconstructions indicating humid and wet conditions during their formation (at least in the recharge area where the deep groundwater originated from). Current change in climate and global warming gives a special importance to this study. During the project the PI made big efforts in studying tufa deposits from a currently extremly dry environments and because of the significance of this question, this study became one of the main research path of the present project. We focussed on the detailed petrographical and geochemical study of the Quaternary tufa deposits in the Kurkur–Dungul stretch, southern Egypt in order to determine their depositional environment, age and their usefulness in the determination of the "Sahara Greening Periods", an important question in connection with human migration out of Africa.

Based on the calculated $\delta^{13}C_{CO_2}$ values and petrography the studied carbonates are tufa deposited from meteogene waters associated with soil and atmospheric CO_2 characterized by low $\delta^{13}C$ values. Observed clotted peloidal mudstone/wackestone, crystalline dendrite cementstone, laminated boundstones, coated plants boundstones, intraclastic rudstones/packstones and micritic dendrite boundstones facies associations suggest deposition in flat environments including stagnant ponds, palustrine and/or lacustrine shores, and at the margin of low-energy continental carbonate depositional system in dammed areas, pools and shallow lakes. Evaporation and related kinetic effects influenced the isotopic composition of the samples causing correlation between their $\delta^{13}C$ and $\delta^{18}O$ values. The stable isotopic composition of the tufa was not significantly influenced by the different facies types.

U−Th dating of the tufa resulted ages between 368 ± 14 ky and 11.7 ± 1.2 ky (MIS 11 and MIS 1). Tufas are getting younger towards lower elevations, indicating a progressive lowering of the water table level with time. The $\delta^{13}C_{tufa}$ values are relatively high (–6.21‰ and –1.42‰), most likely influenced by C4 vegetation, which is common in semi-arid and desert regions. The $\delta^{18}O_{tufa}$ values ($-12.73‰ < \delta^{18}O < -8.87‰$) are low and comparable to the values of tufa deposits from Eastern Europe, where the low $\delta^{18}O$ values are the result of rainout effects due to continentality. Clumped isotope data of nine tufa and one calcite samples infer deposition at 12°C to 34°C, and the $\delta^{18}O$ of the precipitating fluid could had been between −10.7‰ and −6.5‰, similar to the $\delta^{18}O_{water}$ values of the Nubian aquifer in the Western Desert, supporting an Atlantic source of precipitation. These clumped isotope temperatures are the first direct temperature records from the carbonates of the Sahara and the analyses were done with the financial support of the present KH project.

Tufa deposition occurred during both glacials and interglacials. The stable isotope, age, and $T_{\Delta 47}$ data are just loosely associated with humid periods, sapropel events and difficult to match them with Greening Periods of the Sahara. There is no constant lag between tufa deposition and sapropel events, humid periods and speleothem deposition in the studied area. The tufa precipitating water could be relatively old and derived from the Nubian Aquifer, which has been recharged during previous humid climatic conditions. Consequently, the temperature of tufa depositing springs can not be used to record actual climate changes, and rather represent the temperature of the groundwater in the Nubian Aquifer. Differences between $T_{\Delta 47}$ data can be attributable to mixing young waters from the shallow, and fractured basement aquifers, supported by negative calculated $\delta^{18}O_{water}$ values. Tufa deposits can indicate intervals with active springs, instead of humid periods. Regional tufa deposits can be used to study the source of precipitation arrived above the Sahara, which is an important cornerstone of climate studies in North Africa. These results were already presented at conferences and a manuscript is in submission to Quaternary Science Reviews, a Q1 journal:

Kele, S., Sallam, E.S., Capezzuoli, E., Wanas, H., Shen, C.-C., Lone, M.A., Yu, T.-L., Schauer, A., Huntington, K.W. (2020) New data for the "Sahara Greening Periods" from the Western Desert: the tufa carbonates of the Kurkur-Dungul area (Southern Egypt). – Quaternary Science Reviews (submitted) (IF: 4.641)

Kele, S., Sallam, E.S., Capezzuoli, E., Wanas, H., Shen, C.-C., Lone, M.A., Yu, T.-L., Schauer, A.J., Huntington. K.W. (2019) Geochemistry of tufa carbonates from the Western Desert (Southern Egypt). – 34th IAS meeting of Sedimentology, 10-13 September, Rome, Italy

Kele, S., Sallam, E.S., Capezzuoli, E., Wanas, H., Shen, C.-C., Lone, M. A., Yu, T.-L., Huntington, K.W. (2019) Dating and clumped isotope geochemistry of tufa carbonates from the Western Desert (Southern Egypt). – ICIW 2019, Seventh International Clumped Isotope Workshop, January 28-29, 2019, Queen Mary, Long Beach Harbor, Los Angeles, California

Kele, S., Sallam, E.S., Capezzuoli, E., Wanas, H.A., Huntington, K.W. (2018) Facies study and isotope geochemistry of Quaternary tufa and travertine carbonates in the Kurkur–Dungul area (Southern Egypt). 28th Goldschmidt Conference, BOSTON (MA, USA), 2018., Abstracts series.

Kele, S., Sallam, E.S., Capezzuoli, E., Wanas, H.A., Huntington, K.W. (2018) Dél-egyiptomi oázisok (Kurkur-Dungul terület) mésztufaüledékeinek szedimentológiai és geokémiai vizsgálata. 9. Kőzettani és Geokémiai Vándorgyűlés, Mátraverebély-Szentkút, 2018. 09.06-08., Absztrakt kötet (ISBN: 978-963-8221-72-8), pp. 77-78.

2.) Paleotemperature reconstruction of travertines from the Gerecse and Buda Hills (Sándor Kele, László Rinyu)

Paleotemperature reconstruction of Pleistocene travertines from the Gerecse and Buda Hills based on clumped isotopes was an important point of the project with the aim to reconstruct the paleohydrogeology and temporal and spatial changes in the travertine depositing springs. Dated samples available from Kele (2009) served as a basis, but they were completed with new samples as well. Originally, the Δ_{47} analyses were planned at ETH Zürich (Switzerland) and at ATOMKI (Debrecen). However, the ETH laboratory was busy (the planned visit by Stefano Bernasconi was also cancelled), and due to delay in the installation of the ICER Δ_{47} laboratory of the ATOMKI (Debrecen) the first analyses started at University of Washington (Seattle, USA). Finally, in the summer of 2019 the ICER could start the analyses on the travertine samples collected from the Gerecse Hills, while at the same time part of the samples was delivered to the clumped laboratory to Utrecht University with the support of the project.

The Δ_{47} data (from UW Seattle lab) suggest that the T of deposition of Pleistocene travertines of the Buda Hills (e.g. Vár Hill, Gellért Hill, Máriaremete, Barsi út - Rózsadomb, Üröm, Budakalász) varied between 20–37°C, and similarly to the present situation, the springs in the Gellért-Hill and Rózsadomb area had higher temperature than the other paleosprings during the middle Pleistocene. It must be emphasized that these T results are the first direct carbonate-based estimates of paleolfuid temperatures in Hungary. From these material, there is a paper in progress (Kele et al., in prep, a). Sparites and micrites were separately subsampled from Budakalász travertine and also from Tivoli (Italy) and the results revealed that crystal types and inhomogeneity influence the Δ_{47} values causing 10–15°C difference in the calculted temperature between micrite and sparite within a sample (Claes et al., in submisson).

The Δ_{47} of the samples from the Gerecse Hills were measured in three different laboratories and some analyses are still in progress. At Süttő (Gerecse Hills) travertines of the Cukor and Gazda quarries precipitated from the warmest waters (22 and 25°C, respectively), while travertines from the other two quarries formed from cooler waters (Begó-quarry: 11°C, Új-Haraszti-quarry: 18°C). These Δ_{47} results from Süttő (measured at UW Seattle lab) were published by Török et al. (2019) and they are presented below, in a different chapter, together with the new U/Th age data. The rest of the travertine samples of the Gerecse Hills was sent both to the ICER Atomki laboratory and Utrecht University. According to the analyses of Atomki laboratory some of the studied travertine samples from the Gerecse deposited from surprisingly warm water (e.g. Vöröskő: 40±4°C, Alsóvadács: 61±10°C), the other samples formed at rather low- or medium temperature lukewarm waters [e.g. Dunaalmás-Római: 21–25°C (±5–7°C), Kőpite: 25°C (±3°C), Les-hegy: 26°C (±3°C), Süttő, Diósvölgy: 27°C (±2°C)], while some of the calculated temperatures are rather cold [Kiskő-Hegyeskő: 15°C (±5°C), Mogyorósbánya: 12°C (±4°C), Vékonycser: 8°C (±3°C)]. Hoewever, Δ_{47} data from the Utrecht University, performed with the same instrumental setup in some cases resulted in significantly different results from the duplicate samples. The Alsóvadács sample resulted 31°C, a temperature 30°C cooler than the result from Atomki. The sample from Dunaalmás resulted in 14°C which is 7°C cooler than its counterpart measured at Atomki. The Les-hegy sample provided similar temperature (30–31°C) to the one determined at Atomki. The other results from Utrecht (Réz-hegy: 14.6°C, Tata-Öreg-tó: 13°C, Tokod: 18.9°C) are rather low as well, compared to the Atomki data. Due to these currently unexplained discrepancies in the calculated temperatures between the two laboratories, it was still not possible to submit a paper from these data, but the work is in progress (Kele et al., in prep, b). Besides, a paper is in preparation from the U/Th age data and clumped isotope-based paleotemperature records from the travertine of the Vértesszőlős Early Human site (Hungary) and expected to be submitted this year.

Related abstract and manuscripts, whic are being prepared:

Kele, S. és Markó, A. (2018) Paleo-jacuzzi és paleo-dagonya: új adatok a vértesszőlősi lelőhelyekről. KŐKOR Kerekasztal Konferencia, Szeged, 2018. december 7.

Kele, S., Scheuer, Gy., Hong-Wei, C., Shen, C.-C, Schauer, A., Huntington, K.W. (in preparation, a) Reconstruction of paleohydrothermal changes in the Buda Hills based on clumped isotope study.

Kele, S., Ziegler, M., Rinyu, L., Hong-Wei, C., Shen, C.-C, Scheuer, Gy. (in preparation, b) Paleotemperature and $\delta^{18}O$ reconstruction of Pleistocene spring activity in the Gerecse Hills (Hungary) based on clumped isotopes from travertines

Kele, S., Markó, A. Kisné Cseh, J., Shen, C.-C, Wu., C.–C., Bernasconi, S.M., (in preparation) Samuel's paleo–jacuzzi: dating and clumped isotope–based temperature of the Vértesszőlős Early Human site (Hungary)

Claes, H., Török, Á., Erthal, M.M., Soete, J., Mohammadi, Z., Aratman, C., Kele, S., Mindszenty, A., Capezzuoli, E., Swennen, R. (submitted, a) Depositional and diagenetic fabric heterogeneity of Pleistocene to recent travertine and tufa – Impact on stable and clumped isotopes. – Sedimentology (submitted) (IF: 3.244)

3.) Microfacies- and diagenesis study and U-Th dating of the Süttő travertine complex (Ágnes Török, Andrea Mindszenty, Sándor Kele)

Microfacies investigations and diagenesis

At Süttő, based on the geometry of the travertine beds, the antecedent land-surface was variegated consisting of extensive flat sub-horizontal sectors, a more steeply sloping valley, and a southern slope related to the Haraszt Hill. The subhorizontal sectors are characterized by massive and flat laminated lithofacies represented by lacustrine–palustrine depositional environments. The steeply sloping valley provided depositional environment of slope facies, such as the wavy laminated travertines and the phytohermal mounds (Török, 2018; Török et al., 2017; Török et al., 2019).

Travertines are particularly susceptible to early diagenesis (dissolution, reprecipitation, recrystallization, neomorphism etc.) (e.g. Pentecost, 2005; De Boever et al., 2017). Micropetrographical distinction between primary (syndepositional) and later (early diagenetic) fabrics formed as a result of the above processes, is often difficult, sometimes impossible. According to micro-petrographic observations carried out on thin sections of the Süttő samples, the travertine complex was subject to extensive diagenetic overprint including organomineralisation, micritisation, sparitisation and recrystallisation. All these processes were taken place syn-depositionally or right after the travertine formation (Török, 2018; Claes et al., in prep., a). Diagenesis was most intense in the vicinity of the supposed spring orifices, where primary porosity was efficently plugged by abundant calcite cements. Away from the springs where travertine was deposited in either slope- or lacustrine environments, at least part of the primary porosity could survive. This way, however, free channel ways were offerred for later fluids of different composition, to get into contact with the primary precpitates and promote further diagenesis (like dissolution, micritization, recrystallization, neomorphism etc.). Apart from spring-proximity and eventual subaerial exposure, other factors, influencing the vertical and areal distribution of the intensity of diagenetic alteration, are not yet fully understood and will require additional combined micropetrographical and geochemical studies.

U-Th dating

In the Süttő travertine complex 27 samples were collected for dating from different stratigraphic levels of quarries and boreholes covering the entire exposed succession. The sample suitability was evaluated by micro-petrographic observations as well (Török, 2018). The measurements were carried out by High–Precision Mass Spectrometry and Environmental Change Laboratory at National Taiwan University (Taipei, Taiwan). 16 samples of the Süttő travertine area contained thorium from detrital origin ($^{230}Th/^{232}Th < 100$). Therefore, for all samples a detrital correction to the age was applied. The corrected ages were plotted on a map and on a plot of age versus topographic elevation. According to the general rule of classical stratigraphy samples should be younger higher up in the sequence, which is not always the case (e.g. Török, 2018; Török et al., 2019). The somewhat inconsistent age-data-set of part of the Süttő samples may be related to recrystallization, dissolution/reprecipitation, sparmicritization etc. which may all have provided ample opportunity for at least part of the U to be leached out and that is why the age-calculations could have given partly false results (Claes et al., in prep, b). However, the samples represent younger ages towards the Danube, which in line with the terrace stratigraphy of Pécsi (1959) and Kretzoi and Pécsi (1982). These findings were (and will be) published in:

Török, Á., Claes, H., Brogi, A., Liotta, D., Tóth, Á., Mindszenty, A., Kudó, I., Kele, S., Huntington, K.W., Shen, C.-C., Swennen, R. (2019) A multi–methodological approach to reconstruct a dismantled travertine fissure ridge: the case of the Cukor quarry (Süttő, Gerecse Hills, Hungary). – Geomorphology, 345, 106836 (IF: 3.681)

Török, Á., (2018) The anatomy of a Pleistocene travertine body – Sedimetological, Diagenetic and Reservoir studies on the Süttő travertine system (Gerecse Hills, Hungary). PhD thesis, Arenberg Doctoral School, KU Leuven and Eötvös Univ., p. 250.

Claes, H., Török, Á., Erthal, M.M., Soete, J., Mohammadi, Z., Aratman, C., Kele, S., Mindszenty, A., Capezzuoli, E., Swennen, R. (submitted, a) Depositional and diagenetic fabric heterogeneity of Pleistocene to recent travertine and tufa – Impact on stable and clumped isotopes. – Sedimentology (submitted) (IF: 3.244)

Claes, H., Török, Á., Soete, J., Mohammadi, Z., Vassilieva, E., Hamaekers , H., Erthal, M.M., Aratman, C., Cheng, H., Edwards, R.L, Shen, C.-C., Özkul, M., Kele, S.,

Mindszenty, A., Swennen, R. (submitted, b) U/Th dating and open system behaviour of travertine. – Quaternaire, Special Issue on "Multiproxy studies on continental carbonates: palaeoclimates and palaeoenvironments" (submitted) (IF: 0.443)

4.) Fracture-filling calcites of the Pleistocene Süttő travertines (Andrea Mindszenty, Lóránt Bíró, Sándor Kele)

The detailed study of the fracture-filling calcite in the Süttő area had to face a number of unexpected problems, therefore progress was much less than orginally planned. New representative sampling of coarse, tansparent, sparry vein-calcite crystals was rendered impossible because the quarrying activity did not provide good exposures. Apparently those parts of the travertine, which were criss-crossed by the swarm of those spectacular calcite-filled fractures were all excavated during the past years. However, as a result of detailed microtectonic measurements included in Török (2018), Török et al. (2017) and Török et al. (2019), an appropriate, high-resolution structural geological framework is available now, into which both old and new geochemical data on the travertine and also on the calcite-filled fractures (veins) can be fitted. Unfortunately – because of technical difficulties at the isotope-geochemical laboratories in Hungary –, the planned age-dating of the vein-calcite samples could not be underaken within the time-frame of the project. From former samplings in Süttő, two small archive core-fragments from a fracture-filling, banded calcite (taken at Újharaszti quarry) could be recovered. We have analysed these samples for stable O and C isotopes (11 data points from different bands of the vein-filling calcite; sample numbers 1 to 11 from the wall of the fracture towards its open center). As for comparison 14 datapoints of Smekens (2013) measured on the same vein-calcite sample were also taken into consideration. In the evaluation we have included the results of seven additional vein-samples (taken at Gazda quarry, Török, 2018), too.

Fluid inclusion study of the vein-calcites became impossible because of the failure of L. Bíró's application for a grant with the help of which originally he was going to visit the laboratories of KU Leuven, for a training in fluid inclusion studies and for the use of the special instrumentation there. Also, in the meantime the calculation of the precipitation-temperature of the vein-calcites (based on our stable O isotope measurements and on data of Török (2018) and S. Kele's clumped isotope results) has clearly shown that most of the precipitation - even in the fractures - took place ways below ~50 °C, i.e. it turned out that fluid inclusion studies would anyway not have provided any useful contribution to the understanding of the system. As to the distribution of stable O and C isotope data within the banded vein-calcite, we observed that from the oldest towards the youngest bands the $\delta^{18}O$ values were (with some slight anomalies) increasing with time as an indication of possible gradual cooling. The values of $\delta^{13}C$ (all of them negative), however, instead of showing a steady decrease towards the younger bands, reached a minimum in samples 5 and 6 then they became again somewhat heavier (but still negative) and at the end, in sample 11, they changed again for much lighter. In full accordance with Smekens (2013) we think that in addition to an overall cooling of the fluid system in time, our data suggest also an increasing admixture of waters of surface-origin (infiltration from the soil zone?) to the thermal water coming from below. This explains also the karstic dissolution phenomena observed during our field-work; the accumulation of calcite rafts in some of the cavities thus formed and also the occasional Mn-oxide precipitates draping some of the younger bands of the vein-calcites (oxidation and precipitation of Mn dissolved in the uprising thermal water would be readily oxidized on mixing with infiltrating, oxígen-rich surface waters).

5.) Study of fault-related veins from Italy and Turkey (Sándor Kele as participant and consultant of Paola Matera)

There is a strong relationship between tectonic activity, fluid flow and travertine deposition (e.g. Hancock et al., 1999). Geochemistry and isotopic composition of travertine fissure ridges and banded carbonate veins hosted by bedded travertines offer insight into fluid-rock interaction, tectonic activity, palaeoseismicity and paleoclimate research (e.g. Faccenna et al., 2008; Uysal et al., 2009). With the support of the KH project the PI had the possibility to join a research team formed by scientists of University of Bari, University of Florence (Italy) and Pamukkale University (Turkey) including a PhD student Paola Matera (defended her PhD in February 2020). The studies has focussed on fault-related carbonate deposits from three different areas from two countries: 1) The inner Northern Apennines (Bagno Vignoni-Val d'Orcia, Monte Amiata geothermal area, Italy) (Brogi et al., 2020); 2) Iano (Larderello geothermal area, southern Tuscany, Italy); 3) Denizli Basin (Pamukkale geothermal area, SW-Turkey).

The complex structural, geochemical (stable and clumped isotopes) and dating study of travertine deposits and network of banded calcite veins in the Bagno Vignoni-Val d'Orcia area (Italy) allowed us to define the seismo-tectonic setting of this sector of the inner Northern Apennines, demonstrating more broadly the utility of travertine deposits in reconstructing the neotectonics in geothermal areas. The U/Th age data indicated that faulting enhanced the hydrothermal fluid circulation since the middle Pleistocene, in an unchanged tectonic setting, as indicated by the $\delta^{18}O$ signature and temperature of the hydrothermal fluids, which remained stable through time. The activity of the faults continued until the Holocene and still produces seismicity (Brogi et al., 2020).

In the Larderello geothermal area NE-trending transfer zones and their intersections with NW-trending normal faults control the geothermal fluid circulation. The analyzed veins are part of the main conduit of a (mostly NW-oriented) fossil fissure ridge and related fractures. The U/Th datings indicated that fluid circulation forming the banded carbonate veins occurred from 172 ka, at least, to 26 ka. In this time span, the hydrothermal fluid changed in composition and the banded Ca-carbonate veins recorded these variations. Mineralogy, stable and clumped isotope measurements allow the reconstruction of some features (i.e. crystal texture, temperature and CO_2 origin) and the inference of the processes (i.e. pH and T changes and pCO_2 variations) that have controlled the fluid evolution through time (Matera et al., in submission).

These fault-related studies are still in progress, but a paper (Brogi et al., 2020) and a PhD thesis (Matera, 2020) were already publised, other papers are currently being prepared and the results (also from the Turkish sites from the Denizli Basin) were already presented at the IAS meetin in Rome in 2019 September. These findings are (and will be) published in:

Brogi, A., Liotta, D., Capezzuoli, E., Matera, P., Kele, S., Soligo, M., Tuccimei, P., Ruggieri, G., Yu, T.-L., Shen, C.-C., Huntington, K.W. (2020) Travertine deposits constraining transfer zone neotectonics in geothermal areas: an example from the inner Northern Apennines (Bagno Vignoni-Val d'Orcia area, Italy). – Geothermics 85 (2020) 101763 (IF: 3.470)

Matera, P.F., Ventruti, G., Kele, S., Zucchi, M., Brogi, A., Capezzuoli, E., Liotta, D., Yu, T-L., Shen, C.-C. (in submission) Geothermal fluids properties variation in banded Ca-carbonate veins developing in a fault related fissure ridge-type travertine depositional system (Iano, southern Tuscany, Italy). (in submission)

Matera, P.F (2020) Travertine deposition and faulting in extensional setting: a proxy for neotectonic investigation, palaeoseismicity and geothermal fludi flow. – PhD thesis, University Bari, Department of Earth Sciences, 215 p.

Some related abstracts:

Matera, P.F., Ventruti, G., Kele, S., Zucchi, M., Brogi, A., Capezzuoli, E., Liotta, D., Yu, T-L., Shen, C.-C. (in submission) Geothermal fluids properties variation in banded Ca-carbonate veins developing in a fault related fissure ridge-type travertine depositional system (Iano, southern Tuscany, Italy).

Matera, P.F., Kele, S., Ventruti, G., Zucchi, M., Brogi, A., Capezzuoli, E., Ruggieri, G., Liotta, D. (2019) Texture, geochemistry and development of banded veins in travertine depositional systems: implications for tectonic activity and palaeoseismicity reconstruction. – 34th IAS meeting of Sedimentology, 10-13 September, Rome, Italy

Matera, P.F., Kele, S., Ventruti, G., Zucchi, M., Brogi, A., Capezzuoli, E., Ruggieri, G., Liotta, D. (2019) Texture, geochemistry and development of banded calcite veins in travertine depositional systems: implications for tectonic activity and palaeoseismicity reconstruction. – CRUST (Interuniversity Center for 3D Seismotectonics with territorial applications) Workshop, 9-10 July, Perugia, Italy

Matera, P.F., Brogi, A., Kele, S., Capezzuoli, E., Liotta, D., Zucchi, M., Alçiçek, H., Bülbül, A., Alçiçek, M.C. (2019) Crystal morphology and geochemistry of a banded calcite vein from a fault zone (Denizli Basin, Western Turkey). – 34th IAS meeting of Sedimentology, 10-13 September, Rome, Italy

Brogi, A., Liotta, D., Capezzuoli, E., Matera, P.F., Kele, S., Soligo, M., Tuccimei, P., Ruggieri, G., Yu, T.-L., Shen, C.-C., Huntington, K.W. (2019) Travertine deposits and tectonic activity interaction: constraints from Bagno Vignoni-Valdorcia area (inner Northern Apennines, Italy). – 34th IAS meeting of Sedimentology, 10-13 September, Rome, Italy

6.) Paleotemperature reconstruction using soil carbonates from Hungary (Újvári Gábor as PI, Kele Sándor)

One of the major focuses of clumped isotope analyses has been on soil carbonates in the KH project. Last interglacial soil nodules from a loess-paleosol sequence at Dunaszekcső, Hungary were investigated in detail. Stable carbon, oxygen and clumped isotope analyses of MIS 5 soil carbonates revealed that 1) these carbonates formed during the summer season over MIS 5e (or MIS 5c), 2) at 16–20 ºC soil and air temperatures. These values are by 1–5 ºC lower than modern mean summer air temperatures (~21 ºC) of the region and do not match the 2–4°C positive warm season anomalies modeled for East Central Europe between the Last Interglacial (LIG) and present-day in paleoclimate simulations. Soil temperature uncertainties of 1–6 °C and the possibility of MIS 5c formation of the investigated carbonates may account for this proxy-model data discrepancy. These results may imply that the summer seasons were slightly colder in the Carpathian Basin over the MIS 5e than they are today. These findings were published in:

Újvári, G., Kele, S., Bernasconi, S.M, Haszpra, L., Novothny, Á., Bradák, B. (2019) Clumped isotope paleotemperatures from MIS 5 soil carbonates in southern Hungary Palaeogeography, Palaeoclimatology, Palaeoecology 518 (2019) 72–81.

Paleosol carbonates were also sampled in the Paks profile in Hungary from the BA, MB, Mtp and PD1–2 soils, covering an age range of ~300–800 ka. Preliminary stable carbon and oxygen isotope measurements gave $\delta^{13}C$ and $\delta^{18}O$ carbonate values ranging from –9.6 to –3.9 and –10.4 to –6.8‰. These values are used to filter samples for clumped isotope analyses, which have not yet been done. These datasets, together with soil particle size and magnetic measurements, will be used in later paleoenviromental interpretations.

As the KH-17 project evolved, we realized that we should focus our research on mollusc shells from specific warm intervals (Dansgaard-Oeschger events) of the last glacial period. Clumped isotope measurements revealed "background" active season temperatures (AST) (i.e. April/May-September/October) for stadials of the last glacial being in the range of 7–13 ºC, while 16–18 ºC for the GI–5.1 and GI–3 interstadial periods. These warmings in AST are associated with stronger evaporation (^{18}O-enrichment), C4 plant expansion over drier summers (^{13}C-enrichment) and significant drops in mass accumulation rates. These results are not yet published, a related manuscript is in preparation.

7.) Study of freshwater tufa deposits from Hungary (Bódai Barba, Sándor Kele, Mihály Molnár)

The study of freshwater tufa deposits is the PhD topic of Barbara Bódai, but international collaborators were also involved in this part of the project. After mapping, sampling of fossil and recent tufa samples (on plexiglas surfaces) and monitoring studies at the actively precipitating sites together with *in situ* T, pH and EC measurements were done (between 2017 and 2019). Until the end of the project the stable isotope analyses were finished, and two papers are in preparation led by Barbara Bódai, however still some analyses (e.g. clumped isotope and C–14) are in progress. The detailed studies were focussed on the following most important sites were precipitation is active, forming tufa dams: 1) Malom-valley (Felsőörs, Balaton-felvidék); 2) Szalajka-valley (Szilvásvárad, Bükk Mts.); 3) Dobrica-kút (Varbó, Bükk Mts.); 4) Sebesvíz (Bükk Mts.). Anna-cave (Lillafüred, Bükk Mts.) was also sampled and tufas were also analysed for stable isotopes ($\delta^{13}C$: –9.5 to –7.4 ‰ V-PDB and $\delta^{18}O$: 21.5–22.5 ‰ V-SMOW). Interpretation of these data is still in progress and difficult due to the complexity of the tufa beds and mixing of feeding waters fro which the host tufa of the Anna-cave has formed. As from these studies no paper has been published, the results are presented more in detail.

In the Northern part of the Bakony Mts. and in the Balaton Highland area several springs were sampled around Bakonybél and Pénzesgyőr, but no carbonate deposition was observed. At springs around Döbrönte, Farkasgyepű, Németbánya, active carbonate deposition (and water) was sampled for stable isotope analyses, while *in situ* paramaters (T, pH, EC) were determined as well. The Malom-völgy tufa (Alsóörs), which is the biggest and most spectacular tufa deposit was sampled downstream at the tufa dams in order to follow changes. The site was sampled seasonally between 25.11.2017 and 30.11.2019 at 15 sampling stations. Temperature of the feeding spring was almost stable (11.2–12.3°C), showing increasing values during warms seasons downstream, and decreasing ones during colder periods. pH values at the spring varied between 7.13 and 7.49, while they were increased downstream until maximum 8.6 during all seasons due to CO_2 degassing. EC values shown slightly decreasing values downstream (between 841 and 775 μS). Altogether 70 recent tufa samples and 100 water samples have been sampled at the Malom völgy. $\delta^{13}C_{tufa}$ values were between –10.5 and –8.8‰ (V-PDB), $\delta^{18}O_{tufa}$ values between 21.6 an 22.6‰ (V-SMOW), $\delta^{18}O_{water}$ values were between –9.9 and –9.4‰ (V-SMOW), δD values ranged between –70.1 és –66.9 ‰ (V-SMOW).

Similar studies were done in the Szalajka-Valley (Bükk Mts.), where 8 sampling stations were established in 2 km long section. Temperature at the spring varied between 8.3 and 9.4

°C. Temperature values shown increasing values during warm seasons downstream, and decreasing ones during colder periods, however, mixing with the water of Szikla-spring influenced the measured values. At the Szalajka-spring (pH is 6.47–7.48) no tufa deposition was observed, while the pH was increasing downstream in the range between 6.47 to 8.59. EC values show values around 481–494 μS. Altogether 25 tufa and 40 water samples were collected at Szalajka. $\delta^{13}C_{tufa}$ values were between –10.8 and –7.9‰ (V-PDB), $\delta^{18}O_{tufa}$ values between 20.5 an 22.7‰ (V-SMOW), $\delta^{18}O_{water}$ values were between –10.57 and –10.0‰ (V-SMOW), δD values ranged between –72.0 és –70.0 ‰ (V-SMOW).

At Dobrica-kút (Bükk Mts.) 3 sampling stations were installed and 6 tufa and 15 water samples were collected. Temperature at the spring varied between 9.1 and 10.8°C, and this values cooled until 5.5°C in winter, while they increased until 12.1°C in summer downstream. pH values varied between 6.93 and 7.13 at Dobrica-kút and the were increasing downstream until 8.31. EC values show slight downstream decrease in the range between 730 and 581 μS. $\delta^{13}C_{tufa}$ values were between –10.65 and –9.88‰ (V-PDB), $\delta^{18}O_{tufa}$ values between 22.67 and 23.12‰ (V-SMOW), $\delta^{18}O_{water}$ values were between –9.85 and –9.52‰ (V-SMOW), δD values ranged between –68.0 és –67.0 ‰ (V-SMOW).

At Sebesvíz (Bükk Mts.) 2 sampling stations were installed and altogether 5 tufa and 10 water samples were collected. At the spring the temperature varied between 8.3 and 8.9°C during the different seasons, which was cooled down until 3.1°C in cold months, and increased until 11.4°C during warm months. pH value at the spring was 6.48 and increased downstream until 8.42. EC values were slightly decreasing downstream from 504–558 to 424–481 μS. $\delta^{13}C_{tufa}$ values were between –11.15 and –10.19‰ (V-PDB), $\delta^{18}O_{tufa}$ values between 22.3 and 22.83‰ (V-SMOW), $\delta^{18}O_{water}$ values were between –10.16 and –9.19‰ (V-SMOW), δD values ranged between –71.0 és –65.0 ‰ (V-SMOW).

To conclude, the $\delta^{18}O$, δD of water of all the four studied sites were almost constant downstream and seasonally, and evaporation was not significant either. Similarily, there was no obvious downstream or seasonal trend in the $\delta^{13}C$ és $\delta^{18}O$ values of the recent tufa samples. The stable isotope composition of the tufa from the Bükk Mts. and from the Balaton-Highland suggests that the isotopic composition of precipitation was basically the same, or very similar, during their precipitation in both areas. Recent tufa and water samples from the Szalajka-valley and from the Malom-valley were used to test usefulness of existing oxygen isotope thermometer equations. This is an important question, since small deviations from equilibrium (or the use of a not appropriate equation) can introduce significant error into the temperature calculations. Our empirical study resulted that the equation of Craig (1965) gives the best approach to calcuulate the deposition temperature of our tufa samples.

Bódai, B, Kele, S., Czuppon, Gy. (in preparation) A szilvásváradi Szalajka-patak (Bükk, Mo.) és a felsőörsi Malom-patak (Balaton-felvidék, Mo.) mésztufáinak szezonális geokémiai vizsgálata.

C-14 age data of the tufa deposits

The age of the tufa deposits in Hungary is less known, thus, C–14 dating have been started in the ATOMKI AMS C–14 laboratory on 10 samples from the Bükk Mts. (Dobrica-kút, Sebesvíz and Szalajka-völgy). At Dobrica the 4 measured samples show the following ages: < 60 yr, 743–1184 yr, 822–1176 yr, 1521–1824. In the Szalajka-valley, at the Fátyol-vízesés both dated samples were younger than 60 yr. At Sebesvíz 2 samples shown ages younger than 60 yr, while the other three samples were the oldest among the dated samples (2706–2959, 663–1710, 8301–8586 yr). The age younger than 60 yr could be the explained as:

1) the sample is younger than 60 yr; 2) the sample is from the „bomb peak” period; 3) it has the same or higher C‒14 content than the fresh carbonates.

For the determination of the age of a fossil tufa formation, it is necessary to determine the apparent age of the recent samples (zero age), as a recent carbonate deposit might have already significant 14C depletion (expressed as 14C apparent age). Due to lack of organic carbon inbuilt in the samples, 14C was determined from water samples to understand the fresh recent C and old carbonate mixing in a recent tufa sample. However, in some cases we observed that the 14C content of the recent carbonate was higher, than the 14C content of teh water, from which the sample precipitated. This could be explained by the fact that the recent carbonate and water samples were collected not at the same time, while the 14C content of the water has changed, which is important as it might affect the apparent ages. Because of this, a seasonal sampling for C–14 analyses must be continued at the above mentioned three sites. The C–14 data could be published only after these seasonal sampling and dating.

Clumped isotope analyses

In the original project plan clumped isotope analyses were planned on tufa samples. One of the scientific question was the calibration of the clumped isotope thermometer on tufa samples deposited in the low (0–30°C) temperature range. However, the clumped isotope related plans had to face difficulties. There was a huge delay in the installation of the clumped isotope laboratory of ICER Centre (ATOMKI, Debrecen) and the first analyses on the samples related to this project was possible only in September 2019. Meanwhile, the „universal calibration" paper written by Petersen et al. (2019) (in which the PI of this KH projekt was also participated) was published, thus, it looked not straightforward to create another low-temperature clumped isotope calibration line.

Samples for Δ_{47} analyses were sent to both ATOMKI (La Pigna, Sarteano recent tufa samples from Italy and the Szal-2 samples from the Szalajka-valley). Besides, 10 tufa samples dated by the C–14 method were sent for clumped isotope analyses to Utrecht University from Dobrica-kút (4 samples), Sebesvíz (3 samples) and Szalajka-vögy (Fátyol vízesés, 3 samples). Theses analyses are not ready yet, and results and papers are expected later this year. There was also a plan to collect tufa samples for clumped isotope sites from Slovenia. Turkey, Egypt and Italy. The samples were all collected, and the detailed study of the Egyptian tufa samples is in submission. The Slovenian, Turkish samples are not yet measured.

8.) Study of travertine and tufa from Slovakia and Romania (Kele Sándor, Bódai Barbara, Daniella Vieira)

In Slovakia several natural springs still precipitate significant amount of carbonates and the unique feature of the Slovakian thermogene travertine sites is that they frequently form travertine mounds, cones (e.g. Santovka, Dudince, Bojnice, Visné Rucbachy) and their temperature of precipitation is rather low (e.g. Micinské travertíny). The travertine precipitation is most probably connected to post-volcanic activity in Slovakia. With the support (and as a part) of the project the Santovka travertine mound and the inactive mounds around Dudince thermal spa were sampled and their genesis and relationship with paleohydrology and paleoclimate are planned to be studied. For this reason, beside petrography and microfacies description, radiometric (U/Th and C-14) dating, stable- and clumped isotope studies are planned on the ~100 collected samples.

Romania, similarly to Slovakia, is rich in low temperature and saline (high TDS) springs, which actively deposit travertines, and the contributing CO_2 is connected to postvolcanic activity. With the support of the KH project a detailed sampling campaign was completed in Romania in December 2019. Both travertines (Pusztakalán, Borszék, Bálványos, Tusnádfürdő, Korond-, Olasztelek, Kovászna, Feredőgyógy), tufa (Tuszatelke, Esküllő, Pisoaia, Maroshévíz, Feredőgyógy vízesés) were sampled. Altogether 100 travertine and about 40 water samples were collected and analysed. Based on their stable isotope composition, the samples from 4 distinct groups. Tufa samples from Tuszatelke show the lowest $\delta^{13}C$ and $\delta^{18}O$ values (–12‰ <$\delta^{13}C$<–10‰, V-PDB) and together with the tufa from Esküllő, they overlap with the Hungarian tufa deposits, which means that there was no significant differences in the $\delta^{18}O$ of the precipitating meteoric water betwen the two countries. Tufa samples from Maroshéviz show higher $\delta^{13}C$ values (around 1–3‰), while their $\delta^{18}O$ values vary between 16 and 21‰ (V-SMOW). The precipitating water here is a thermal water which cools down downstream and precipitates „thermal" tufa further from the thermal Spa of Maroshéviz. Travertine samples with similar carbon and oxygen isotope composition were collected from the inactive Feredőgyőgy and Pusztakalán travertine mounds and from the Feredőgyógy water fall. The inactive spring mound at Olasztelek forms isotopically the third group together with recent and fossil samples collected from Borszék, and the $\delta^{13}C$ values of this group are the highest among the studied samples (between +8‰ and +11‰), clearly indicating a heavy carbon input soewhere in the system, while the $\delta^{18}O$ values are in the „normal" 20–25‰ (V-SMOW) range. The fourth group is made of the carbonate samples from Korond (and Kovászna), which is a spectacular site, where estremely saline, low temperature springs precipitate reddish travertine, but also pure aragonite at the Csiga-Hill, a perfect place to study aragonite-water oxygen isotope fractionation. The $\delta^{13}C$ of these samples are also in the thermoge range of Pentecost (2005) and vary between +3 to +9 ‰ (V-PDB), but their $\delta^{18}O$ is extremely high between 35–45‰ (V-SMOW). The water samples collected at Korond are also spectacular, they are positive, reaching even the extremely high +9.37 ‰ (V-SMOW), most probably due to the high TDS content.

At this moment, no paper is being prepared from the Slovakian and Transylvanian samples, because the isotope analyses have just finished and as a next step clumped isotope analyses with U-Th dating are planned on some selected samples. The Slovakian travertines are the PhD topic of Daniella Vieira, while the Romanian tufa related studies belong to the PhD research of Barbara Bódai (both of them are PhD students of the PI).

9.) Universal clumped isotope calibration efforts (international collaboration) (Sándor Kele as participant)

The clumped isotope composition (Δ_{47}) of carbonate-derived CO_2 is a function of formation temperature of carbonate, thus, it can be used in paleoclimate researches, or infer burial or diagenetic conditions. However, observed inter-labory differences in the measured T-Δ_{47} relationship is a serious problem, which makes difficult to compare Δ_{47} values from different laboratories. The absolute abundance of heavy isotopes in the universal standards VPDB and VSMOW (defined by the following four parameters: R^{13}_{VPDB}, R^{17}_{VSMOW}, R^{18}_{VSMOW} and λ) impact calculated Δ_{47} values. With the help of the KH-17 projcet the PI has participated in an international collaboration to investigate whether use of updated and more accurate values for these parameters could remove observed inter-laboratory differences in the measured T–Δ_{47} relationship (Petersen et al., 2019). This was a huge effort made by the clumped isotope community to create a „universal" calibration, reprocessing 14 published calibrations from 11 different laboratories. With the KH-17 support it was possible for the PI to attend the personal discussions at ICIW 2019 (Seventh International Clumped Isotope workshop, Los Angeles, California, USA) and to visit the clumped isotope laboratory of John Eiler, at Caltech

(Pasadena, California), where the clumped isotope method was invented. These findings were published in a highly ranked Q1 journal and the some months old paper is already highly-cited:

> Petersen, S.V., … Kele, S., .Winkelstern, I.Z. (2019) Effects of Improved ^{17}O Correction on Inter-Laboratory Agreement in Clumped Isotope Calibrations, Estimates of Mineral-Specific Offsets, and Acid Fractionation Factors. – Geochemistry, Geophysics, Geosystems, DOI: 10.1029/2018GC008127 (IF: 2.95**)**

10.) Factors controlling clumped isotopes and $\delta^{18}O$ values of hydrothermal vent calcites (Sándor Kele)

Travertines can form within a relatively wide range in nature. The pH and growth rate dependence is known for oxygen isotopes and it was also postulated for clumped isotopes. Using recently forming travertine samples (pH: 6.1–7.5, T: 33–100°C) from Italy, Turkey and Hungary, it was studied and tested, whether pH (in addition to temperature) can influence the carbonate clumped isotope composition or not. The results show that pH-related effects are mostly small for Δ_{47} in the sub-surface environment at low pH and that high mineral growth rates control the magnitude of this disequilibrium. These findings were published in a highly ranked Q1 journal:

> Kluge, T., John, M.C., Boch, R., Kele, S. (2018) Assessment of factors controlling clumped isotopes and $\delta^{18}O$ values of hydrothermal vent calcites. – Geochemistry, Geophysics, Geosystems, 19:6, 1844–1858 (IF: 2.98)

11.) Clumped isotope temperatures from dolomites (Sándor Kele)

Although it was not mentioned in the original project plan, during the KH-17 project the PI has participated in dolomite-related studies as well. These findings are not detailed here but they are partly related to the project and the support of the project is acknowledged in the two Q1 papers published from the results with the participation of the PI.

> Lukoczki, G., Haas, J., Gregg, J. M., Machel, H. G., Kele, S., John, C.M. (2020) Early dolomitization and partial burial recrystallization: A case study of Middle Triassic peritidal dolomites in the Villány Hills (SW Hungary) using petrography, carbon, oxygen, strontium and clumped isotope data. – International Journal of Earth Sciences *(accepted)* DOI:10.1007/s00531-020-01851-7 (IF: 2.295)

> Lukoczki, G., Haas, J., Gregg, J.M., Machel, H.G., Kele, S., John, C.M. (2019) Multi-phase dolomitization and recrystallization of Middle Triassic shallow marine–peritidal carbonates from the Mecsek Mts. (SW Hungary), as inferred from petrography, carbon, oxygen, strontium and clumped isotope data. – Marine and Petroleum Geology 101, 440-458. (IF: 3.538)

Summary

This project was the first in Hungary, which applied the novel and still continuously developing clumped isotope method to calculate the depositional temperature of travertine, tufa, vein calcite, paleosoil carbonates, mollusc shells and dolomites as well. Although some of the aspects of the original research plan had to be slightly modified, these changes allowed the PI to deal with other (sometimes more) important samples and scientific questions and, despite the relatively short length of the project, several Q1 papers were published and the scientific outcome was maximized.

Funding from the KH/NKFIH project allowed us to reconstruct some details of paleohydrothermal changes in the Buda and Gerecse Hills based on the studied travertines. Important monitoring and geochemical studies (including C–14 dating) have started on Hungarian and foreign tufa (Transylvanian) deposits. Based on soil-carbonates MIS–5 paleotemperatures were reconstructed using clumped isotopes and study of mollusc shells from specific warm intervals of the last glacial period were done as well. Detailed dating and clumped isotope analyses on Egyptian tufa deposits helped us to reconstruct the „Greening periods" in the Western Desert of the Sahara, a crucial question in connection with human migration out of Africa. A the Süttő travertine complex, the age of the travertine, and the impact of diagenesis and fracture filling calcites were studied in detail. Slovakian and Romanian low-temperature travertine deposits, special types of travertine mounds were also sampled as a topic of two PhD students involved into the project. Studies on fault-related veins and travertine fissure ridges from Italy and Turkey emphasized the significance of geochemistry of these deposits in fluid-rock interaction, tectonic activity, palaeoseismicity and paleoclimate research. The PI participated in the universal clumped isotope calibration project. The research has a high impact and the resulted calibration equation will be used by future clumped isotope-based papers. Clumped isotope study of recently forming carbonates from Italy, Turkey and Hungary revealed that pH-related effects are mostly small for Δ_{47} in the sub-surface environment at low pH and that high mineral growth rates control the magnitude of this disequilibrium. Finally, clumped isotopes studies on dolomites from the Mecsek Mts. and Villány Hills allowed to reconstruct multiphase dolomitization, recrystallization processes.

In summary, we firmly believe that the project fullfilled its goals. With the support of NKFIH several papers were published, and many others are in submission or in preparation. These papers are expected to be published during 2020–2021. Due to the project, strong international collaborations are built and the project allowed the PI to participate important meetings, workshops, international field trips and cover the expenses of the clumped isotope analyses. For this reason, the PI is grateful to NKFIH for the support provided.

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