PRELIMINARY RESULTS ON PALEOCLIMATE RESEARCH IN MECSEK MTS, HUNGARY

Gabriella Koltai[1,4], Sándor Kele[2], Gergely Surányi[3], Beáta Muladi[4], Ilona Bárány-Kevei[4]

[1]Hertelendi Laboratory of Environmental Studies, Institute of Nuclear Research, Hungarian Academy of Sciences, P.O.Box 51, 4001 Debrecen, Hungary, koltaig@atomki.hu

[2]Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budaörsi út 45, 1112 Budapest, Hungary, keles@geochem.hu

[3]Department of Geophysics and Space Science, Eötvös Loránd University, Pázmány P. sétány 1/C, 1117 Budapest, Hungary, surda@pangea.elte.hu

[4]Department of Climatology and Landscape Ecology, University of Szeged, P.O Box 653, 6701 Szeged, Hungary, keveibar@geo.u-szeged.hu, muladi.beata@gmail.com

The geochemical analyses of karst springs and their freshwater carbonate deposits provide an opportunity to reconstruct past climate changes. Nevertheless, there are still very few paleoclimate records obtained from freshwater carbonate deposits in Hungary. The present study focuses on some recently depositing freshwater tufa sites and two caves located in Mecsek Mts (Southern Hungary) as possible sources for Holocene paleoclimate research. Both carbonate and water samples were collected for stable isotope analyses in June and August 2011 and a monitoring programme was started in October 2011 at five sites. The stable isotope analyses of the rock samples reflect the effect of continentality and suggest strong soil zone CO_2 contribution.

1. Introduction

Terrestrial carbonate deposits (travertines, freshwater tufas and speleothems) are of particular importance in paleoclimatological, paleoenvironmental and geological studies. Speleothems, such as stalagmites, stalactites and flowstones, are a rich archive of terrestrial paleoclimate information (e.g., Wang et al. 2001) particularly since they offer the dual advantages of being closely tied to the mean hydrological balance and being a nearly ideal material for high precision U/Th disequilibrium series dating. Recent studies have proved that freshwater carbonate deposits, such as travertines and tufas can also be used in paleoenvironmental reconstruction (Andrews 2006, Lojen et al. 2009, Cremaschi et al. 2010) and their geochemical composition can be correlated with climate records gained from lake sediment, ice-cores (Stuiver et al. 1995) and marine sediments (Imbrie et al. 1984). The effects of global climate changes can be studied on them, since these deposits reflect local paleo-precipitation patterns and preserve key information on the paleoenvironment, as well.

In Hungary, in spite of the existence of large karst areas such studies have been delayed and there are still very few paleoclimate records obtained from terrestrial carbonate deposits (Kele et al. 2006; Kele 2009; Siklósy et al. 2009). Five carbonate depositing springs and two caves are taken under scrutiny in Western and Eastern Mecsek for paleoclimatic investigation. Our main aim is to reconstruct the Holocene paleoclimate of the study areas by doing a comparative geochemical analysis of these carbonate deposits. In this paper we would like to present the preliminary results of the research we started in the summer of 2011.

2. The study area

Mecsek Mountains is divided into Western and Eastern Mecsek. The karst areas of Western Mecsek are built up by well-karstifiable, Triassic rocks (Lapisi Limestone Formation, Zuhányai Limestone Formation, Csukma Dolomite Formation) in which numerous small caves, dolines and karst springs were formed. Three of the regularly studied springs (Kánya Spring, Anyák Spring and Dagonyászó Spring) and both caves are located here. In Eastern Mecsek karstic rocks are of Jurassic origin and have less suitable petrographic characteristics for karstification and speleogenesis. Two springs sites (Csurgó Spring and Pásztor Spring) have been monitored here (Fig. 1).

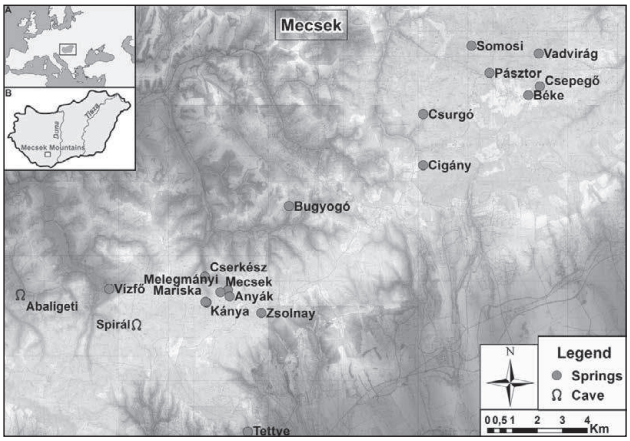

Figure 1. The study area (based on 1:10,000 scale topographic map in EOTR (Uniform National Mapping System of Hungary).

3. Methods

Recently deposited freshwater tufa samples were collected for stable isotope ($\delta^{18}O$, $\delta^{13}C$) analyses in June and August 2011 at 10 sites and water samples at 17 sites. In case of five springs monthly observations have been carried out for 10 months since October 2011. Two measurement points were set at each spring sites where the basic physicochemical parameters of water (pH, conductivity, temperature) were measured *in situ* once every month by using a WTW device. Water samples were collected in 100 ml bottles for determining alkalinity which were analysed within 48 hours by acid-based titration with 0.1 M HCl. Two meteorological parameters (air temperature and relative humidity) were also recorded at each measurement points at the time of measuring the other parameters.

Figure 2. The drilling site and the drilling core of Anyák Spring, Western Mecsek.

Besides, core drillings were carried out at three places on the surface (Anyák Spring, Csurgó Spring and Pásztor Spring, Fig. 2) and in case of two speleothems in Abaliget and Spirál caves.

The stable isotope analyses were performed at the Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, Hungary. Oxygen and carbon isotopes of bulk carbonate were determined using a Finnigan delta plus XP mass spectrometer. Oxygen and hydrogen isotopic measurements of water samples were done on LGR LWIA-24d liquid water isotope analyser. Isotopic compositions are expressed in the traditional δ notation in parts per thousands (‰) relative to VPDB ($\delta^{18}O$, $\delta^{13}C$) and VSMOW ($\delta^{18}O$, δD). Reproducibilities are better than ±0.2 ‰ for the $\delta^{18}O$ and $\delta^{13}C$ values of carbonates and ±0.2‰ for the $\delta^{18}O$ and ±0.6‰ for the δD values of water.

4. Results and discussion

4.1. Physicochemical water parameters

Water temperature shows a regular seasonal pattern reflecting the variation in air temperature, being higher in summer and lower in winter. Due to the moderating effect of the karst aquifer the amplitude of changes were 4.6 °C, 4.0 °C, 3.8 °C, 3.0 °C and 2.9 °C at Csurgó Spring, Pásztor Spring, Anyák Spring, Kánya Spring and Dagonyászó Spring, respectively. The reason behind this high amplitude in the case of Csurgó Spring is that there is no specific spring source, water appears in the stream bed and consequently it starts to equilibrate with surface temperature. The highest temperatures were recorded in April and July and the lowest in October and January.

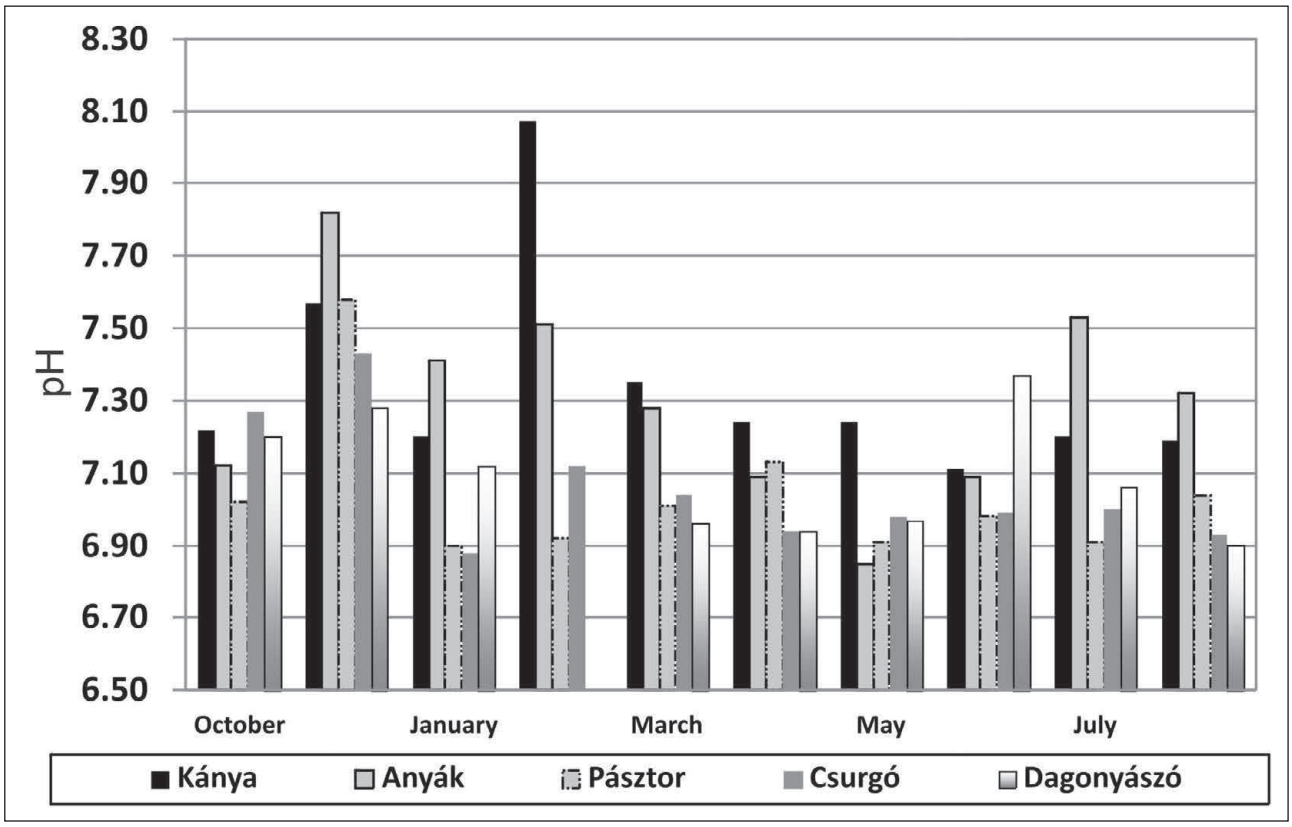

Figure 3. Monthly changes of pH, 2011–2012.

Downstream the water temperature increased in summer and decreased in winter. The seasonal amplitude rose to 14.5 °C, 18.1 °C, 19.1 °C, 8.9 °C and 7.8 °C, respectively.

Alkalinity had a similar seasonal pattern as water temperature. It was higher from late spring to autumn and lower from winter to early spring. Similarly to electric conductivity, alkalinity decreased downstream due to tufa deposition. The highest values of electric conductivity were measured at Anyák and Kánya springs (655–766 µS/cm and 702–755 µS/cm, respectively), while Pásztor Spring was usually characterised by much lower values (570–680 µS/cm). This is probably due to the differing geological characteristics of the limestone aquifer. Similarly low values were recorded at other springs in the same area (Vár Valley and in Óbánya Valley).

Contrary to electric conductivity and alkalinity, pH values gradually increase downstream. According to Kano et al. (1999) the seasonal variation of pH is characterized by high winter and low summer values, since more uptake of soil-originated CO_2 intensifies the dissolution of $CaCO_3$ and reduces the pH of the water. Soil pCO_2 is the highest from July to September and changes of the Ca^{2+} content, alkalinity and pH usually follow its seasonal variation with a delay of 1 or 2 months (Kano et al. 1999; Kawai et al. 2006). In Mecsek Mts. the highest pH levels were measured at the end of November and a second peak was observed at the end of January. Except for Pásztor and Kánya springs a pH values slightly increased at the beginning of summer (Fig. 3) and decreased in August.

Usually, Anyák and Kánya springs are characterized by higher pH levels than the other springs, most likely owing to differing aquifer conditions.

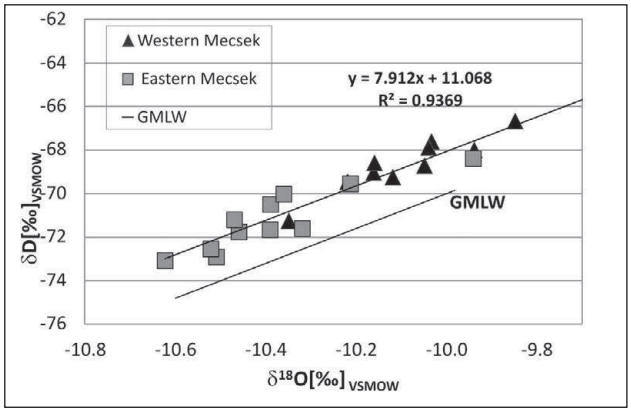

Figure 4. Stable isotopic composition of spring waters.

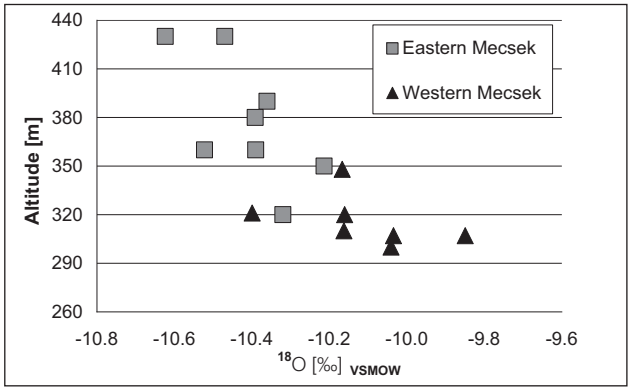

Figure 5. $\delta^{18}O$ values of spring waters plotted against sample altitude.

4.2. Stable isotopes

Stable isotope analyses of the 17 karst springs revealed unambiguous differences between Eastern and Western Mecsek (Fig. 4). The possible cause of this difference could be the so-called "altitude effect" or the "amount effect". The springs of Eastern Mecsek are located at higher altitude and have their catchment areas at higher elevation than the ones in Western Mecsek. Therefore, the investigated springs in Eastern Mecsek are characterized by more negative isotope values (Figs. 4 and 5).

At some springs (e.g., Anyák Spring) monthly differences can be observed in the isotope composition of the karst water, reflecting seasonal changes in precipitation $\delta^{18}O$. Nevertheless, isotopic values change little ($\delta^{18}O$: 0.4‰ both at the spring and at the tufa site). The δD and $\delta^{18}O$ data of the studied springs fit the Global Meteoric Water Line, indicating their meteoric origin. The mean values are -69.8‰ and -10.2‰, respectively.

The observed difference between Eastern and Western Mecsek in the $\delta^{18}O$ data cannot be seen in case of tufa samples which can be a result of the difference in water temperatures in which the tufa calcite forms. Unfortunately, all the parameters were recorded once a month so we can only estimate the mean water temperature at the places of tufa deposition. Kinetic effects might occur, as well. Further investigations are needed to understand this difference. In order to monitor the $\delta^{18}O$ and $\delta^{13}C$ changes of recently depositing freshwater tufas, glass substrates were put at the measurement points in September 2012. Unfortunately, we have no reportable results yet.

Table 1. Stable isotopic composition of carbonates.

Tufa-depositing springs	$\delta^{18}O$ ‰ (VPDB)	$\delta^{13}C$ ‰ (VPDB)	Altitude (m)
Kánya Spring	-8.6	-9.9	307
	-8.7	-11.2	307
Anyák Spring	-9.3	-9.9	320
	-9.4	-10.1	319
	-9.2	-10.6	318
Pásztor Spring	-9.1	-11.1	430
Tettye Spring	-9.3	-10.7	208
	-9.1	-10.4	208
Zsolnay Spring	-8.6	-10.0	348
Dagonyászó Spring	-9.2	-11.6	321
Mecsek Spring	-8.5	-11.4	310
Bugyogó Spring	-8.7	-9.4	350
Vadvirág Spring	-8.6	-9.0	360
	-8.6	-9.2	360
Csurgó Spring	-8.9	-11.0	320

Table 1 shows the isotope composition of the tufa samples. The $\delta^{13}C$ values of our tufa samples range between -9.0‰ and -11.6‰ (VPDB) with a mean value of -10.3‰, suggesting strong soil-zone CO_2 contribution. Comparing our stable isotope data with the database established by Andrews et al. (1997) the samples from Mecsek Mountains are similar to the tufas collected in Poland and in the Dinaric Karst concerning $\delta^{18}O$ values, reflecting the effect of continentality in contrast to the tufas collected from Western-Europe.

The freshwater tufa cores were quite porous and therefore were embedded in epoxy amber. The most recent part of the speleothem core from Abaliget Cave was micro-drilled with approximately 1 mm intervals and samples for Hendy-test were prepared which suggest that the speleothem core is suitable for further investigations. The stable isotope measurements of the freshwater tufa and speleothem cores are still in progress. We intend to use U/Th method for the dating of these samples. We tried ^{14}C for dating the tufa cores, however further measurements are needed in order to interpret the results correctly.

5. Conclusions

The stable isotope analysis of the tufa-depositing streams suggests that these waters are of meteoric origin. A significant difference was found between the two study areas, Eastern and Western Mecsek most probably as a result of difference in the elevation of the catchment areas.

The seasonal variation of the different physicochemical parameters of water was observed during the monitoring period. It also became evident that pH increases, while alkalinity and electric conductivity decreases downstream. The downcurrent changes of water temperature depend on air temperature.

Stable isotope analysis of bulk carbonate samples showed that the isotopic composition of these deposits reflect the effects of continentality and strong soil-zone CO_2 contribution by C3 vegetation.

Acknowledgements

The authors express their gratitude to the reviewers for their useful comments that improved the quality of the paper. Special thanks goes to A. Demény who allowed us to analyse these samples at the Institute for Geological and Geochemical Research. A. Boros and K. Kármán are acknowledged for performing the stable isotope measurements.

References

Andrews JE, 2006. Paleoclimatic records from stable isotopes in riverine tufas: Synthesis and review. Earth-Science Reviews 75, 85–104.

Andrews JE, Riding R, Dennis PF, 1997. The stable isotope record of environmental and climatic signals in modern terrestrial microbial carbonates from Europe. Paleography, Paleoclimatology, Paleoecology 129 (1–2), 171–189.

Cremaschi M, Zerboni A, Spötl C, Felletti F, 2010. The calcareous tufa in the Tadrart Acacus Mt. (SW Fezzan, Libya): An early Holocene palaeoclimate archive in the central Sahara. Paleography, Paleoclimatology, Paleoecology 287 (1–4), 81–94.

EOTR (Uniform National Mapping System of Hungary) 1:10,000 scale topographic maps. FÖMI (Institute of Geodesy, Cartography and Remote Sensing), Budapest.

Imbrie J, Hays JD, Martinson DG, McIntyre A, Míx AC, Morley JJ, Pisias NG. Prell WL, Shackleton NJ, 1984. The orbital theory of Pleistocene climate: support from a revised chronology of the marine $\delta^{18}O$ record. In: Berger AL, J Imbrie, JD Hays, J Kukla, J Saltzman (Eds) Milankovitch and Climate, Part 1, Reidel, Hingham, Mass. 269–305.

Kano A, Kambayashi T, Fujii H, Matsuoka J, Sakuma K, Ihara T, 1999. Seasonal variation in water chemistry and hydrological conditions of tufa deposition of Shirokawa, Ehime Prefecture, southwestern Japan. Journal of the Geological Society of Japan 105 (4), 289–304.

Kawai T, Kano A, Matsuoka J, Ihara T, 2006. Seasonal variation in water chemistry and depositional processes in a tufa-bearing stream in SW-Japan, based on 5 years of monthly observations. Chemical Geology, 232, 33–53.

Kele S, 2009. Édesvízi mészkövek vizsgálata a Kárpát-medencéből: paleoklimatológiai és szedimentológiai elemzések. (Paleoclimatological and sedimentological analyses of travertines from the Carpathian Basin.) PhD Thesis, Eötvös Loránd University, Hungary (in Hungarian).

Kele S, Demény A, Bajnóczi B, Korpás L. Kovács-Pállfy P, Medzihradszky Zs, 2006. Paleoenvironmental evaluation of the Tata Travertine Complex (Hungary), based on stable isotopic and petrographic studies. Acta Geologica Hungarica, 48, 1–31.

Lojen S, Trkov A, Scancar J, Vázquez-Navarro JA, Cukrov N, 2009. Continuous 60-year stable isotopic and earth-alkali element records in a modern laminated tufa (Jaruga, river Krka, Croatia): Implications for climate reconstruction. Chemical Geology, 258, 242–250.

Siklósy Z, Demény A, Szenthe I, Leél-Őssy Sz, Pilet S, Lin Y, Shen CC, 2009. Reconstruction of climate variation for the last millenium in the Bükk Mountains, northeast Hungary, from a stalagmite record. Időjárás 113 (4), 24–263.

Stuiver M, Grootes M P, Braziunas TF (1995) The GISP2 18 Record of the Past 16.500 Years and the Role of the Sun, Ocean, and Volcanoes. Quaternary Research, 44, 341–154.

Wang YJ, Cheng H, Edwards RL, An Z, Wu JY, Shen CC, Dorale JA, 2001. A high-resolution absolute-dated late Pleistocene monsoon record from Hulu Cave, China. Science, 294, 2345–2348.