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PRELIMINARY STUDIES OF FRESHWATER TUFA DEPOSITS IN MECSEK MTS., HUNGARY

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Summary: The geochemical and stable isotope 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 five recently depositing freshwater tufa sites (Anyák Spring, Csurgó Spring, Pásztor Spring, Dagonyászó Spring and Kánya Spring) located in Mecsek Mts. (Southern Hungary) as possible sources for Holocene paleoclimate research. Carbonate samples were collected for stable isotope analyses in June and August 2011 and a monitoring programme was started in October 2011. The stable isotope analyses of the rock samples reflect the effect of continentality and suggest strong soil zone CO_2 contribution.

Key words: paleoclimatology, freshwater tufa, stable isotopes, water chemistry, seasonal variation

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 sediments, 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). Small freshwater tufa sites are common in Mecsek Mountains and their sampling is easily achievable. As tufas are laminated, long-term monitoring of water parameters is the best way to study the characteristics of their deposition and the way how they preserve climate signals. This paper presents the main freshwater tufa depositing streams chosen for a paleoclimate reconstruction and the preliminary results of our monthly observations.

2. MATERIALS AND METHODS

2.1. The study site

The tufa-bearing streams are located in Western and Eastern Mecsek. The geological structure of Western Mecsek is characterized by an anticline with an eastern-western line of strike. The rocks of the anticline are particularly stressed, fragmented and moved by faults (Barta and Tarnai, 1999). In Western Mecsek karstic rocks geologically belong to one single block, however, on the surface they can be found in three different zones. Three of the studied objects, Anyák (Anyák-kútja), Dagonyászó and Kánya springs, are located on the largest karstic block (Fig. 1). The area is 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. The karstic rocks of Eastern Mecsek are of Jurassic origin and have less suitable petrographic characteristics for karstification and speleogenesis. Two springs sites, Csurgó and Pásztor springs, have been investigated here (Fig. 2).

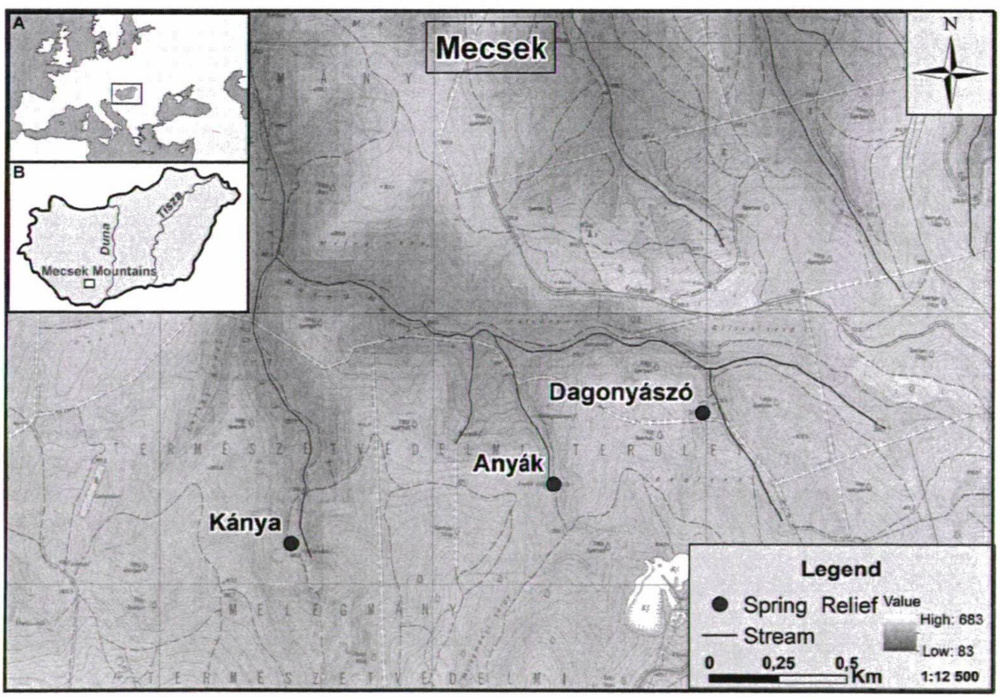

Fig. 1 The study area in Melegmányi Valley, Western Mecsek Mts., Hungary (based on 1:10,000 scale topographic map in EOTR (Uniform National Mapping System of Hungary)

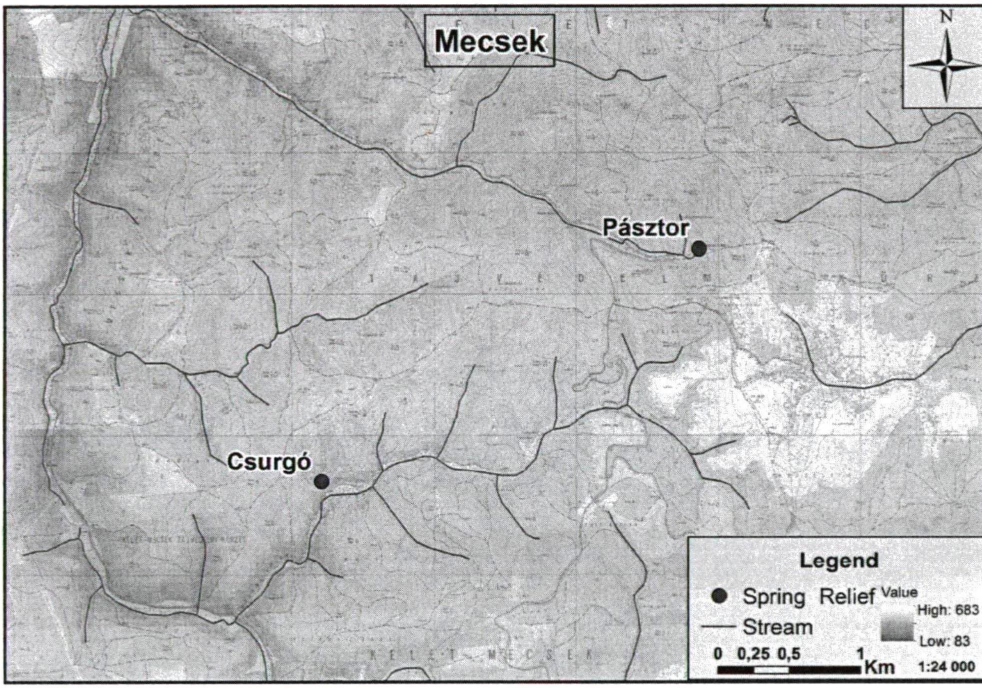

Fig. 2 The study area in Eastern Mecsek Mts., Hungary (based on 1:10,000 scale topographic map in EOTR (Uniform National Mapping System of Hungary)

2.2. Methods

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* on a regular basis 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.

Recently deposited carbonate samples were collected for stable isotope ($\delta^{18}O$, $\delta^{13}C$) analyses in June and August 2011 at 10 spring sites. The stable isotope analyses were performed at the Institute of 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. Isotopic compositions are expressed in the traditional δ notation in parts per thousands (‰) relative to PDB ($\delta^{18}O$, $\delta^{13}C$). Reproducibilities are better than ±0.2 ‰ for the $\delta^{18}O$ and $\delta^{13}C$ values of carbonates.

3. RESULTS AND DISCUSSION

3.1. The tufa sites

The tufa depositing streams in Mecsek Mountains are usually small creeks having water discharge ranging from 0.02 to 1.4 l/sec. The first tufas usually appear 10-80 m from the spring site and form along the streams until the water loses its ability to deposit freshwater carbonates. In all cases water flows along a single course from the spring at the observed parts, however due to the changes of water flow rate and evaporation, some parts can dry out during the warm season. During summer the surfaces of the tufas are covered by moss, algae and cyanobacteria (Fig. 3).

Fig. 3 Moss and algae cover the freshwater mini waterfall of Anyák Spring, May 2012

The karst water of Anyák Spring (Anyák-kútja) deposits the largest freshwater tufa dams in Mecsek Mts. However, the first fluvial crusts appear 20 m from the beheading of the spring, the largest dams are to be found 200 m further. The deposition rate becomes higher due to changes of surface morphology, and therefore a series of dams and cascades were formed on steep stream bed. Kraft et al. (1986) suggests that the thickness of the dams is about 8 m. The height of the deposits sometimes exceeds 1-1.5 m. The limestone fills the complete cross section of the narrow valley.

Kánya and Mariska springs are located in Nagy-Mély Valley and have a 400 m long riverine tufa deposition along the valley. The first tufa deposits appear approximately 10-15 metres from Kánya Spring before the water of Mariska springs flows into the stream. A series of smaller and larger dams can be found along the riverbed for 400 m owing to the continuous outgassing of CO_2 (Fig. 4).

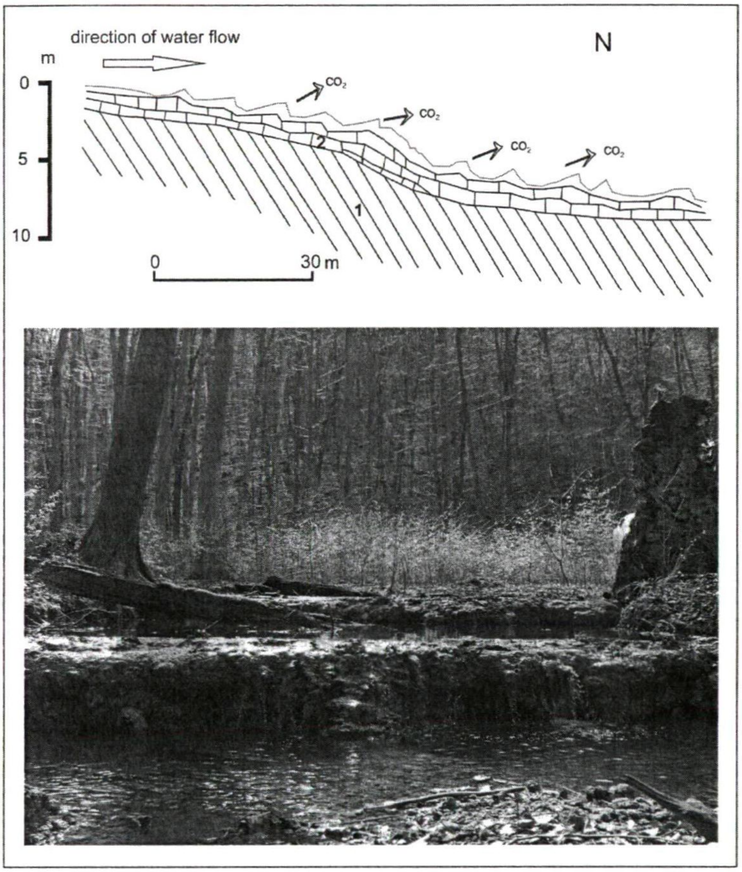

Fig. 4 Tufa dam deposition at Kánya Spring as a consequence of continuous CO_2 degassing. 1: bedrock 2: recently depositing freshwater tufa

The fan-shaped tufa deposits at Dagonyászó Spring are quite porous and contain a high amount of organic material. The first deposits are little (0.1 m high) waterfalls forming 15-20 metres far from the spring.

Csurgó Spring is one of the most well-known sites in Eastern Mecsek. The spring has no specific vent; the water simply appears in the stream bed. Several mini-dams and two large cascades make the site spectacular. Unfortunately, the freshwater tufa cascades were destroyed by falling trees during a storm in July 2012.

Pásztor Spring is the uppermost spring of Vár Valley. Some small sinkholes are known on its catchment area (Karft and Scheuer 1988). The supersaturated water led to the formation of both a fan-shaped valley floor infilling and several larger tufa dams. Freshwater tufas are quite consistent.

3.2. 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. 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 early spring (Fig 5.). Similarly to electric conductivity, alkalinity decreased downstream which is most probably 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 due to the differing quality of the limestone aquifer. Similarly low values were recorded at other springs in Vár Valley and in Óbánya Valley.

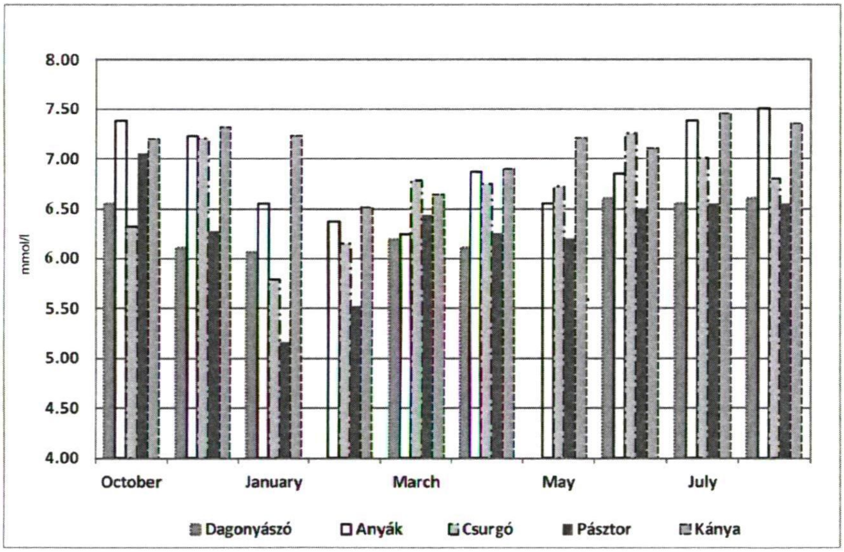

Fig. 5 Variation of alkalinity at the springs, 2011-2012

Contrary to electric conductivity and alkalinity, pH values gradually increase downstream. According to the scientific literature (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). 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 pH values slightly increased at the beginning of summer (Fig. 6) 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.

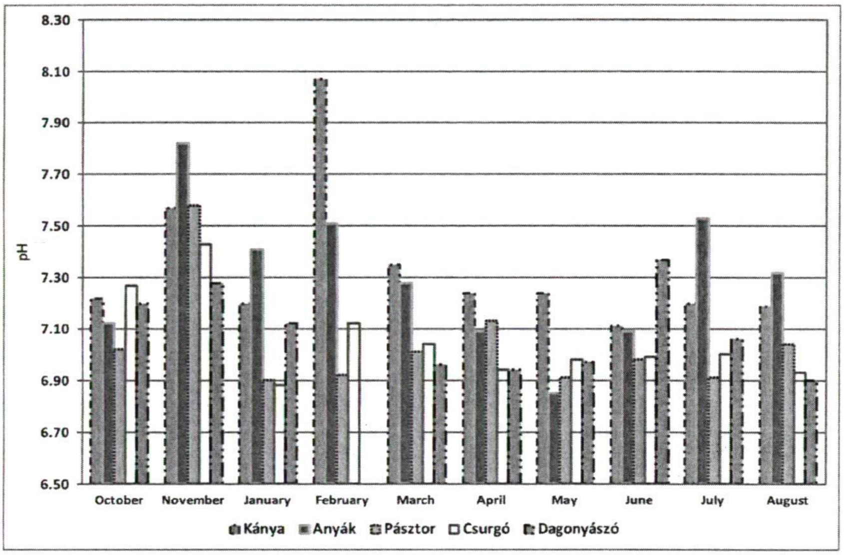

Fig. 6 Monthly changes of pH, 2011-2012

3.3. Correlation coefficients between the variables and the different springs

Alkalinity, electric conductivity, pH, water temperature and air temperature were analysed. Air temperature was recorded at each measurement sites when the physicochemical parameters of water were measured. Large correlation coefficients were found between water temperature and air temperature with a correlation coefficient R^2=0.463 on a 0.01 significance level. At the tufa depositions a negative correlation was experienced between water temperature and alkalinity (R^2= -0.475) which is most probably due to the temperature dependence of dissolved CO_2 and the changes in the amount of available CO_2 during infiltration.

Concerning pH a connection was found between Csurgó and Kánya and between Csurgó and Pásztor springs on a 0.05 significance level. The relationship was even stronger between Kánya and Pásztor springs (R^2=0.855 on a 0.01 significance level). The changes of electric conductivity were similar in case of Anyák and Dagonyászó, Anyák and Kánya, Csurgó and Kánya springs, on a 0.05 significance level. Interestingly, no correlation was found between Dagonyászó and Kánya or Anyák and Csurgó springs. Regarding alkalinity only Anyák and Kánya springs correlated with each other on a 0.05 significance level. This might be due to similar aquifer conditions, however, further research is needed in order to understand the relationship between the observed springs.

3.3. Stable isotopic composition of carbonates

15 rock samples were collected at ten spring sites in the summer of 2011. Table 1 shows the isotopic composition of the tufa samples. The $\delta^{13}C$ values of our tufa samples are isotopically light and range between -9.0 ‰ and -11.6 ‰ (V-PDB) 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) and Andrews (2006), 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 compared to the tufas collected from Western-Europe (Fig. 7).

Table 1 The isotopic composition of freshwater tufa samples from Mecsek Mts., Hungary

Tufa-depositing springs	$\delta^{18}O$ ‰ (V-PDB)	$\delta^{13}C$ ‰ (V-PDB)	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

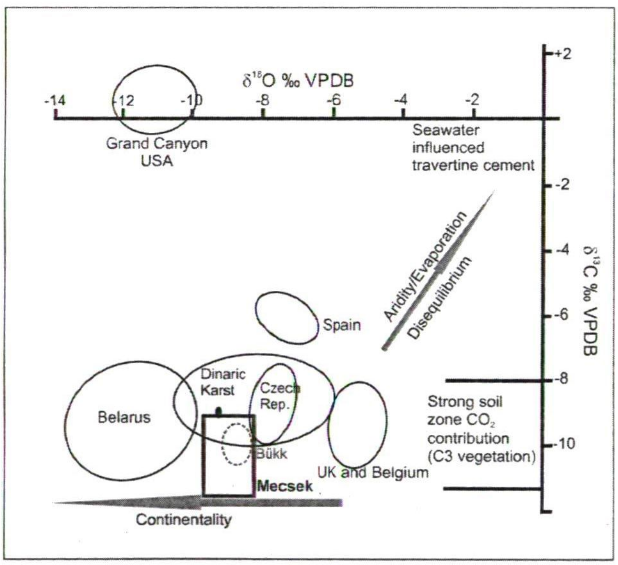

Fig. 7 Isotopic cross plot of freshwater tufa deposits from Mecsek Mts. with other European samples (after Andrews 2006)

4. CONCLUSIONS

During our research we have studied some of the major freshwater tufa depositions of Western and Easter Mecsek Mts., Hungary for 10 months. 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 variation of water temperature depends on air temperature. Statistically significant relationship was found between water and air temperature and between water temperature and alkalinity. Correlation was discovered between some springs concerning the fluctuation of the various parameters, nevertheless regarding pH and conductivity, significant connection was only found in the case of Kánya and Csurgó springs.

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