

Calculation of temperature and $\delta^{18}\text{O}$ of depositing water by measured $\delta^{18}\text{O}$ of recent travertines deposited from the Budapest thermal karst water

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Linear correlation between the temperature and measured $\delta^{18}\text{O}_{\text{water}}$ of Budapest thermal karst water system presents an opportunity to estimate both the temperature and $\delta^{18}\text{O}$ of the depositing water if only the $\delta^{18}\text{O}_{\text{travertine}}$ is known.

Our observations on several Hungarian groundwaters and travertines deposited recently from them resulted that $\delta^{18}\text{O}$ data of travertines originating from cold karst water and thermal water of porous aquifer are close to the "experimental" curve presented by Friedman and O'Neil (1977). Conversely, the calculated fractionation factors of thermal karst waters significantly deviate from the experimental curve following an "empirical-curve" ($R^2 = 0.99$) as: $1000 \cdot \ln \alpha = (2.76 \cdot 10^6)/T^2 - 1.31$.

The empirical equations calculated by this "empirical-curve" as $T_{\text{water}} = (25 - \delta^{18}\text{O}_{\text{trav}})/0.22$ and $\delta^{18}\text{O}_{\text{water}} = 0.186 \cdot \delta^{18}\text{O}_{\text{trav}} - 14.22$ are usable only for the Budapest thermal karst regime and only for recent travertines. Extrapolation of these equations to the past and use them to estimate the deposition temperature of paleo-travertines needs detailed information of the paleoclimate and age of travertine.

Key words: oxygen isotope fractionation, travertine, thermal karst water, empirical equation

Introduction

Studies of climate variations in the geological past can significantly contribute to reliable estimations of expected future climate trends. Valuable paleoclimate records for continental areas are provided by non-marine carbonates, including lacustrine sediments, travertines, freshwater tufa deposits and speleothems.

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Their formation temperatures can be calculated using various methods, and among them conventional carbonate-water paleothermometry (McCrea 1950; Epstein et al. 1953; Kim and O'Neil 1997) is one of the most frequently used one. The disadvantage of this method is that it requires knowledge or estimation of the oxygen isotope composition of the water from which the carbonate was precipitated.

Final prospecting goal of our investigations is to develop a combined method for paleoclimate and water temperature estimations from $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data of paleo-travertines. Our paper presents the results of the first steps of this investigation as development of a method for calculation of both temperature and $\delta^{18}\text{O}$ of parent water in the Budapest thermal karst water system using only measured $\delta^{18}\text{O}$ of recent travertines deposited at the orifice of thermal springs/wells. Further steps will need additional hydrogeological, geothermal and dating studies, too.

Method of calculations

In case of calcite-water isotopic equilibrium stable oxygen isotope composition of travertines ($\delta^{18}\text{O}_{\text{trav}}$) is controlled by the temperature (T) of deposition and by the $\delta^{18}\text{O}$ of the travertine-depositing thermal water ($\delta^{18}\text{O}_{\text{water}}$). $\delta^{18}\text{O}$ fractionation factor between travertine and water ($1000 \cdot \ln \alpha$) depends on the temperature and can be calculated using the equation of Friedman and O'Neil (1977) as:

$$1000 \cdot \ln \alpha = 1000 \cdot \ln [(1000 + \delta^{18}\text{O}_{\text{trav}})/(1000 + \delta^{18}\text{O}_{\text{water}})] = (2.78 \cdot 10^6)/T^2 - 2.89 \quad (1)$$

The fractionation factor values calculated by Equation 1 as a function of $10^6/T^2$ (where T is given as °K) are presented in Fig. 1 ("experimental curve"). The validity of this curve was tested by measuring temperatures and oxygen isotope compositions of waters and recently precipitated carbonates in Hungary. These "empirical" values (points in Fig. 1) were compared with the experimental ones calculated by the known temperature of deposition. In optimal case these two values should be the same, i.e. the points should fit to the "experimental-curve".

Origin of groundwater and recent travertine data

Detailed studies of stable oxygen and carbon isotope compositions of travertines have been accomplished in the Institute for Geochemical Research, Hungarian Academy of Sciences (Budapest) (Kele et al. 2008, 2011; Demény et al. 2010). Additional travertine $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data were provided by the ATOMKI (Institute of Nuclear Physics, Debrecen) (Szöőr et al. 1991; Hertelendi and Svingor 1996) and by the measurements of Deák (1986) at the Institute for Environmental Physics in Heidelberg.

Groundwater isotope data (Fórizs et al. 2007; Deák et al. 2010) were used to determine the isotope-hydrogeological features of the Budapest thermal karstwater system. The other groundwater isotope data were collected from archive publications (Deák 1979; Hertelendi 1995).

Evaluation of data

Recent Hungarian travertines were divided into three groups by the type of depositing water as:

- karst thermal waters (K/thermal) with temperature $>20\text{ }^{\circ}\text{C}$
- cold karst waters (K/cold) with temperature $<20\text{ }^{\circ}\text{C}$
- thermal waters of the porous Pannonian aquifer on the Great Hungarian Plain.

Figure 1 presents that in case of Pannonian thermal waters and cold karst waters the experimental and the empirical fractionation ($1000\cdot\ln\alpha$ values are similar to each other.

Conversely, the empirical fractionation factors of thermal karst waters (20 to 95 $^{\circ}\text{C}$) significantly deviate from the experimental curve following the equation ($R^2 = 0.99$):

$$1000\cdot\ln\alpha = (2.76\cdot 10^6)/T^2 - 1.13 \quad (2)$$

Equation 2 presents that the coefficient of T^{-2} ($2.76\cdot 10^6$) is similar to the experimental value ($2.78\cdot 10^6$) so the two curves are parallel to each other. This fact suggests that the deviation is less dependent on temperature than the additional constant as -1.13‰ and -2.89‰ , respectively. This difference of 1.76‰ ($= 2.89-1.13$) means about $8\text{ }^{\circ}\text{C}$ higher measured temperature of deposition as the "experimental" value calculated by Eq. 1 as it was also shown by Kele et al. (2008, 2011) in case of recently forming travertines in Egerszalók (Hungary) and Pamukkale (Turkey). Using the experimental curve of Kim and O'Neil (1997) as $1000\cdot\ln\alpha = 18030/T - 32.42$ (dashed line in Fig. 1) the difference will be even higher between the calculated and empirical fractionation factors.

International comparison

The validity of the empirical oxygen isotope fractionation curve established for the Hungarian thermal karst waters was investigated using available data set from other karst areas abroad (Table 1). Values of travertines deposited at the nearest place to the orifice were selected ruling the disturbing effect of secondary fractionation out (Kele et al. 2008, 2011).

The method of calculation was the same as in the case of recent Hungarian travertines. The differences of the calculated and experimental $1000\cdot\ln$ data (Fig. 2) were found in other areas to be similar to the Hungarian thermal karst travertines. Two points out of 13 (No. 11 and 12 in Table 1, from Colorado and

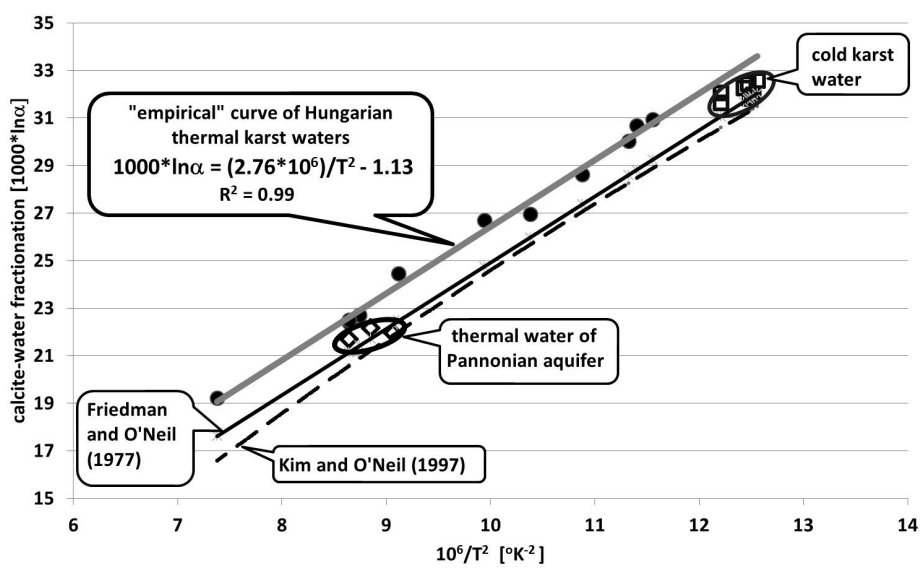


Fig. 1 "Empirical-curve" by detected calcite-water oxygen isotope fractionations of recent travertines in Hungary compared to "experimental-curves" of Friedman and O'Neil (1977) and Kim and O'Neil (1997)

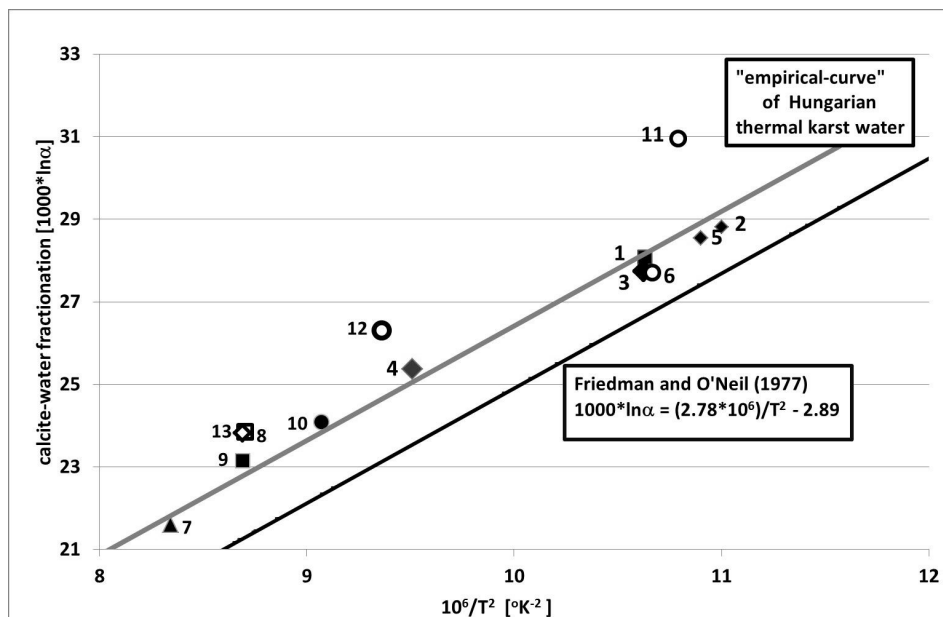


Fig. 2 Comparison of fractionation factors established in Hungary with data of other karst areas. No. of points are listed in Table 1

Table 1
Foreign data of recent travertines and their parent thermal karst waters

Area	Local name	Source of data	Number on Fig 2	Water temperature		$\delta^{18}\text{O}_{\text{water}}$ (measured) [%] _{SMOW}	$\delta^{18}\text{O}_{\text{trav}}$ (measured) [%] _{SMOW}	1000* $\ln\alpha$ (travertine/water)	
				[°C]				Calculated by measured $\delta^{18}\text{O}$	Friedman and O'Neil (1977)
Nevada	Devils Hole	Coplen 2007	1	33.7		-13.5	14.6	28.1	26.7
Tenerife	Los angeles	Demény et al. 2010	2	28.5		-8.1	20.9	28.8	27.7
Tenerife	Madre del Agua	Demény et al. 2010	3	33.8		-8.1	19.8	27.7	26.6
Karahayit	Kirmizi Su spring	Kele et al. 2011	4	51.3		-7.8	17.7	25.4	23.5
Pamukkale	Jandarma spring	Kele et al. 2011	5	30.1		-8.8	19.9	28.5	27.1
Pamukkale	Beltes 2 spring	Kele et al. 2011	6	33.2		-8.5	19.3	27.7	26.8
Yellowstone Park	Angel Terrace Spring	Fouke et al. 2000	7	73.2		-18.3	4.0	22.5	20.3
Yellowstone Park	Narrow Gauge 3	Chafetz and Lawrence 1994	8	66.0		-18.3	5.4	23.9	21.3
Yellowstone Park	Narrow Gauge 5	Chafetz and Lawrence 1994	9	66.2		-17.9	5.1	23.1	21.3
Viterbo	Le Zitelle	Chafetz and Lawrence 1994	10	59.0		-6.7	17.5	24.1	22.3
Colorado	Durango	Chafetz and Lawrence 1994	11	31.4		-14.2	16.8	31.0	27.1
California	Pagosa Spring	Chafetz and Lawrence 1994	12	53.8		-12.7	13.6	26.3	23.1
California	Bridgeport	Chafetz and Lawrence 1994	13	66.2		-16.7	7.0	23.8	21.3

California) are lying far from the "empirical-curve" presenting even higher deviations from the "experimental-curve".

Estimation of temperature and $\delta^{18}\text{O}$ of depositing water by $\delta^{18}\text{O}$ of recent travertines in the Budapest thermal karst water system

The "empirical-curve" (Eq. 2) can serve as an excellent tool to estimate the $\delta^{18}\text{O}$ of recent travertines being deposited from thermal karst waters in Hungary, but the inverse problem (i.e. estimation of temperature of deposition and $\delta^{18}\text{O}$ of water from the measured $\delta^{18}\text{O}$ of travertine) needs additional information about the hydrogeological system.

Such information is available in the Budapest thermal karst water system. Linear correlation between the temperature and measured $\delta^{18}\text{O}$ of water (Fig. 3)

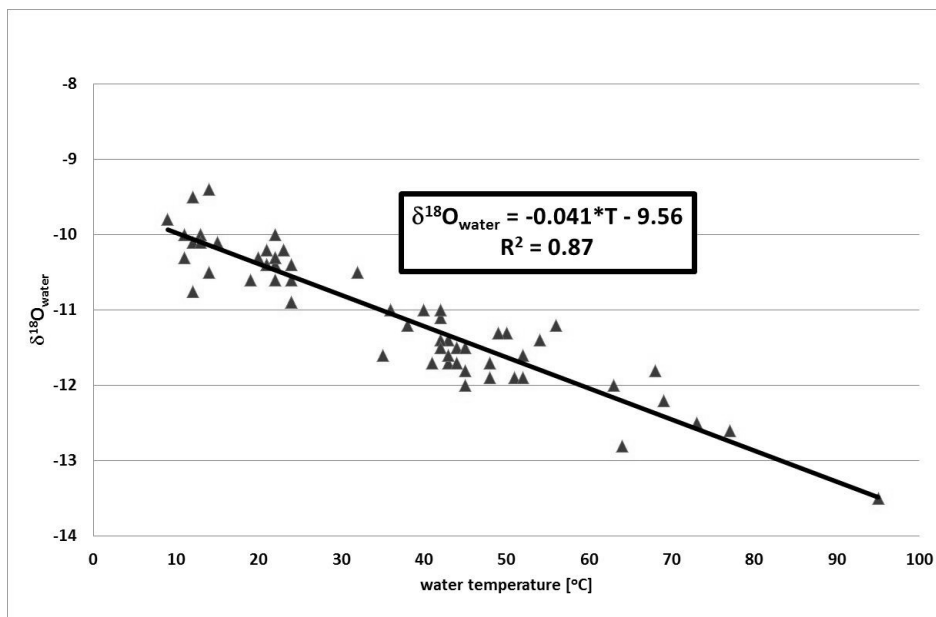


Fig. 3
Correlation between the temperature and $\delta^{18}\text{O}$ of the Budapest thermal karst water system

presents an opportunity to estimate both temperature and $\delta^{18}\text{O}$ of water from $\delta^{18}\text{O}$ of recent travertines.

First step: $\delta^{18}\text{O}$ values of possibly deposited travertines were calculated by the measured $\delta^{18}\text{O}$ and temperature data of water of Budapest thermal karst system, using the "empirical" fractionation curve (Eq. 2) for the Hungarian thermal karst waters (Fig. 4). The seven travertines to be measured (triangles in Figure 4) are – of course – close to the curve.

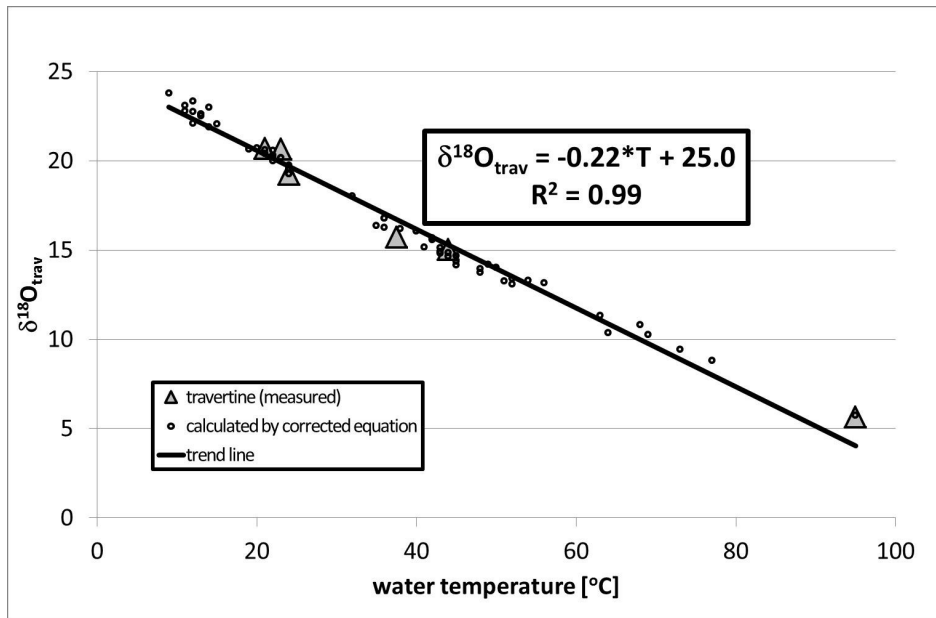


Fig. 4
Estimated and measured $\delta^{18}\text{O}$ of recent travertines in the Budapest thermal karst water system

The temperature of depositing karst water can be calculated from the $\delta^{18}\text{O}$ of travertine by arranging the equation of regression line in Figure 4 as:

$$T_{\text{water}} [\text{°C}] = (25 - \delta^{18}\text{O}_{\text{trav}}) / 0.22 [\text{‰}] \quad (3)$$

Combining the Eq. 3 with equation of Figure 3, the stable oxygen isotope ratio of depositing water can be calculated as:

$$\delta^{18}\text{O}_{\text{water}} = 0.186 * \delta^{18}\text{O}_{\text{trav}} - 14.22 \quad (4)$$

These empirical relations are usable only for the Budapest thermal karst regime and only for the recent travertines. Extrapolation of these equations to the past and their use to estimate the deposition temperature of paleo-travertines needs detailed information on the paleo-hydrogeology, paleoclimate and age of travertine.

Conclusion

The linear correlation between temperature and measured $\delta^{18}\text{O}_{\text{water}}$ of the Budapest thermal karst water system provides an opportunity to estimate both the temperature and $\delta^{18}\text{O}$ of the depositing water if the $\delta^{18}\text{O}$ of travertine is known. Studies on recent Hungarian travertine deposits and their parent waters

were used to calibrate the experimentally determined fractionation curve of Friedman and O'Neil (1977). The calculated oxygen isotope fractionation factors between travertine and water of recent travertine deposited from Hungarian thermal karst waters deviate significantly from the "experimental curve" following an "empirical-curve" ($R^2 = 0.99$) as $1000 \cdot \ln \alpha = (2.76 \cdot 10^6)/T^2 - 1.13$. The empirical equations calculated by this "empirical-curve" as $T_{\text{water}} = (25 - \delta^{18}\text{O}_{\text{trav}})/0.22$ and $\delta^{18}\text{O}_{\text{water}} = 0.186 \cdot \delta^{18}\text{O}_{\text{trav}} - 14.22$ are usable only for the Budapest thermal karst regime and only for the recent travertines. Extrapolation of these equations to the past and their use to estimate the deposition temperature of paleo-travertines needs detailed information on the paleo-hydrogeological conditions, paleoclimate and age of travertine.

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