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BRACKETING THE AGE OF FRESHWATER CARBONATE FORMATION BY OSL DATING NEAR LAKE KOLON, HUNGARY

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Abstract

Freshwater carbonates are unique depositions in the centre of the Carpathian Basin, with debated origin and age. Their formation on the sand covered area of the Danube-Tisza Interfluve is mainly related to lakes appearing in low lying interdune areas from time-to-time. Carbonate deposition is governed by various processes, but in general it can be traced back to climatic and concomitant surface and subsurface hydrological variations. Therefore marl, limestone and dolomite layers can be a marker of environmental change. To identify the type of environmental change they may indicate absolute or numerical ages are needed. In previous studies this issue has been addressed by the means of radiocarbon dating. In the present study we attempted to bracket the age of freshwater carbonate formation with the help of optically stimulated luminescence dating and compared our results to radiocarbon data from the literature. In general, the luminescence properties of the investigated samples proved to be suitable for determining the age of the bedding and covering sediments. OSL dates confirmed previous interpretations that freshwater carbonate formation in the area could have a peak around 10,5 ka. However, the termination of the deposition could not be unambiguously determined at the present stage of the analysis. The compound geomorphology and sedimentology of the study area call for further investigations.

Keywords: OSL dating, freshwater carbonates, environmental change, blown sands

INTRODUCTION

In the Carpathian Basin freshwater carbonate deposits may occur at various locations, but have mostly been reported from the blown sand covered area of the Danube-Tisza Interfluve (DTI). The extension and thickness of occurrences is highly variable as a consequence of the mosaic landscape and the complex formation of the deposits (Sümegi et al., 2011). The source of the carbonates, precipitating and accumulating in the form of hard and compact limestone and dolomite benches is debated (Fügedi et al., 2008; Sümegi et al., 2011). Nevertheless carbonate formation has been extensively studied and the major processes have been identified by Molnár et al. (1981). Deposition can traditionally be related: 1) to groundwater fluctuation and consequent precipitation of Ca/Mg rich salts from pore water above the fluctuation zone and 2) to shallow lakes where either CO_2 distraction by plants or time-to-time desiccation can lead to extensive carbonate formation (Molnár and Botz, 1996; Fügedi et al., 2008). However, based on palinological data, Sümegi et al. (2011) have shown that carbonate formation can also occur at deeper oligotrophic stages of lake evolution. Nevertheless, each interpretation underlines the importance of climatic changes and parallel alteration of the hydrological regime. Besides, they agree in that the Ca-content of lake carbonates is higher than those precipitating from groundwater (Molnár and Botz, 1996; Fügedi et al., 2008).

The time of carbonate formation has been also debated, as previously it was primarily related to drier and warmer periods of the Holocene, namely the Boreal Phase (Mucsi, 1963). Based on radiocarbon measurements on herbivorous gastropod shells enclosed by carbonate deposits at a typical limestone exposure, Jenei et al. (2007) have proved that major carbonate formation started at around 13,0-11,5 ka (9500-11000 cal BC) and terminated at 6,9 ka (4900 cal BC), thus they pushed the peak of carbonate formation to the colder climate of the Late Glacial. These results were reinforced by the extensive study of Sümegi et al. (2011) at another site in the basin of Lake Kolon, using also radiocarbon dating. Based on their study, carbonate rich marls were formed between 13.6 ka and 10.5 ka (11,393–11,621 cal BC and 8311–8455 cal BC) with a peak around 11 ka.

Freshwater carbonate formation cannot be restricted to the Late Glacial however, as it was already suggested by Jenei et al. (2007), who identified carbonate formation up till around 3.3 ka (1300 cal BC). A similar result can be deduced from the study of Sipos et al. (2009) from another site on the DTI where they dated the blown sand bedding of a carbonate rich lacustrine layer by using optically stimulated luminescence (OSL) to 3,8 ka and the organic rich cover of it by using radiocarbon to 3,5 ka (1500 cal BC).

The aim of the present research is to provide further data for the time of carbonate formation on the DTI by performing OSL measurements on sediments below and above freshwater carbonate layers. These measurements provide also the possibility to compare the results of different numerical dating methods and therefore to achieve a more robust interpretation for the timing and environment of carbonate formation in the Carpathian Basin.

STUDY AREA

Lake Kolon is situated on the western edge of the sand hills of the DTI in a former channel of the Danube (Fig. 1). The elevated, central territory of the DTI had been the alluvial fan of the Danube throughout most of the Pleistocene (Pécsi, 1967). The shift of the river to its present day N-S direction is estimated to occur 30-40 ka ago, and generally explained by the subsidence of the Baja and Kalocsa depressions southwest of the area (Jaskó and Krolopp, 1991). The westward translation of the Danube was presumably continuous, and a final phase of this process could be the formation of a 5-6 km wide valley on the western edge of the alluvial fan (Fig. 1). Lake Kolon, and the study site is situated in this relatively deep lying area. The age of the channel and the termination of fluvial activity have not been determined yet, though radiocarbon dating of lake sediments led Sümegi et al. (2011) to the conclusion that lacustrine sedimentation started at around 27 ka (25 000 cal BC).

After the Danube had left the area, fluvial processes were overtaken mostly by eolian activity, especially intensive during the Last Glacial Maximum (Borsy, 1977; Borsy, 1987; Lóki et al., 1994). In these circumstances the basin was time-to-time covered by sand sheets. Consequently, a hummocky landscape appeared with wind blown depressions and residual

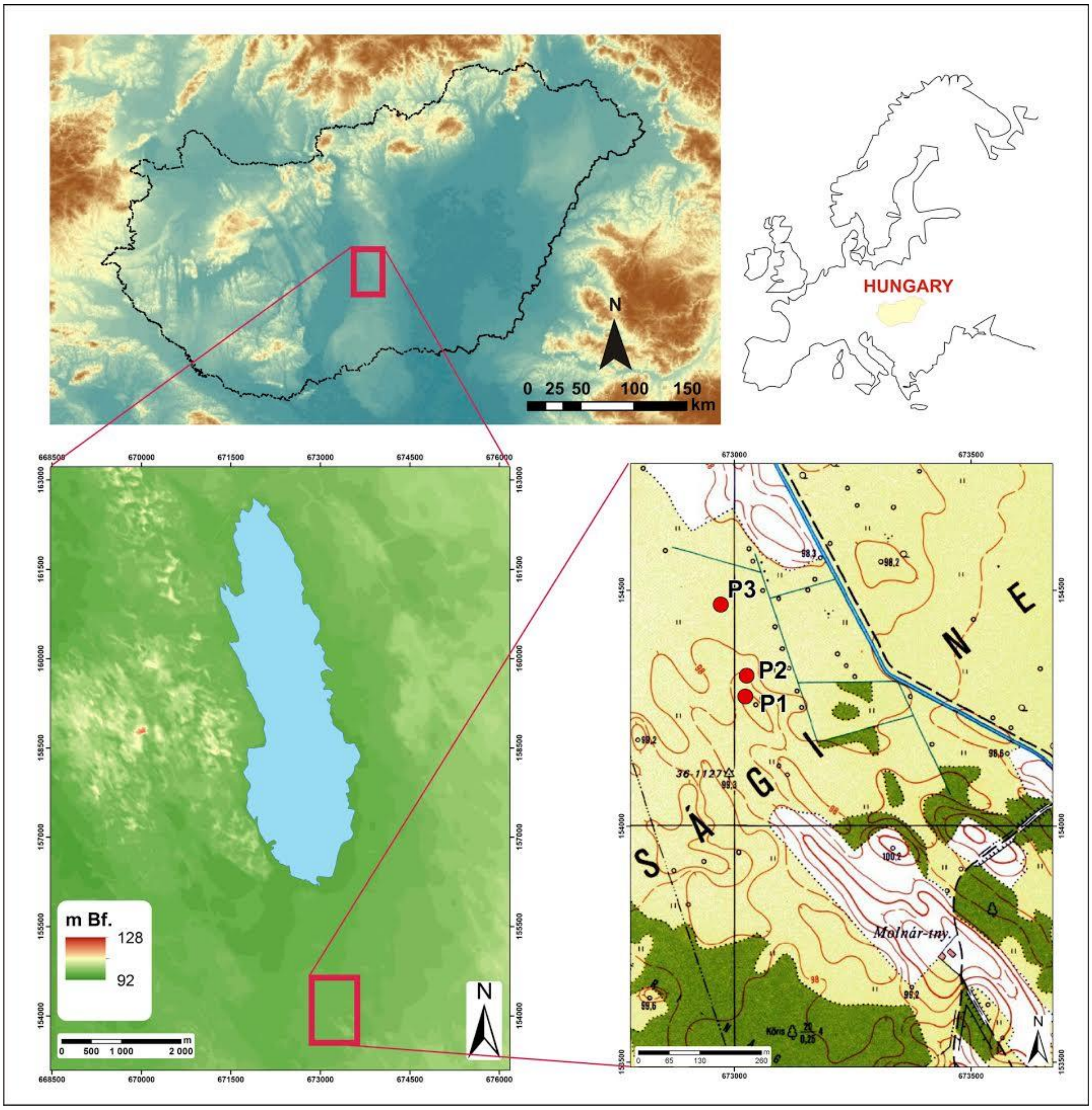

Fig. 1 Location and topography of the study site near Lake Kolon

ridges, which favoured the development of a mosaic network of wetlands and shallow lakes, adequate for freshwater carbonate formation (Sümegi et al., 2011). However, as a result of height differences between sub-basins considerable spatial and temporal variations can be presumed in terms of carbonate formation. Spatial variability is reinforced by the study of Pécsi et al. (2014), when using high resolution drilling and ground penetrating radar for the delineation of dolomite platforms and carbonate rich layers in the area.

OSL dating was performed south of the present day lake (Fig. 1). At the study site 3 sampling points were identified, the lowest and the highest being at 97.5 m and 99.0 m asl., respectively. The geomorphology of the area is compound, a deflational basin can be seen at sampling point P3, while point P2 and point P1 are located at the foot and on the top of a NW-SE direction, relatively small positive form, interpreted as a left behind wing fragment of a larger parabolic dune, situated SE of the form (Fig. 1).

MATERIALS AND METHODS

Sedimentary features were mapped at the study site as described by Pécsi et al. (2014) by using hand drills and a Pürckhauer soil sampler. After revealing the spatial extension of carbonate rich layers 2 drillings were made to collect OSL samples by using Eijkelkamp type undisturbed sampling cylinders (Fig. 2). At sampling point P3 the bedding of the freshwater dolomite was sampled from an artificial exposure, using the same cylinders. The aim of sampling was to collect sediments of relatively high sand content from below and above the very fine grained carbonate layers. In all, 9 samples were taken, each weighing about 200 g. From layers, in which only low sand content was presumed on the basis of orienteering drills, double samples were collected. The processing of these samples was started separately, however, in case it was necessary they were merged to receive an adequate amount of material for dating. In one case even the doubled sample did not yield enough datable grains (OSZ872/873).

Sample preparation was based on the techniques proposed by Aitken (1998) and Mauz et al. (2002) for coarse grain sample treatment. First the samples were wet sieved to separate the 90-150 µm grain size fraction, the typical grain size interval for blown-sand sediments. Subsequently, samples were subjected to repeated acid treatments (HCl and H_2O_2) to remove their usually high carbonate and moderate organic matter content. The quartz content was divided from other minerals by heavy liquid separation (2.62 and 2.68 cm^3). In order to clean quartz, and to remove any remaining feldspars a 45 min HF etching was applied. Grains were adhered to stainless steel sample holding discs by using silicone spray and a 4 mm mask, chosen as a compromise between signal intensity and the available low amount of material.

The absorbed dose since deposition, termed as the equivalent dose (D_e) was determined by using the single aliquot regenerative-dose (SAR) protocol (Murray and Wintle, 2000; Wintle and Murray, 2006), on a RISØ DA-15 automated TL/OSL system with a beta dose rate (Sr/Y) of 0.105±0.002 Gy s^{-1} at the time of measurements. Preheat temperatures were set between 200-240 °C depending on the results of dose recovery preheat plateau tests, performed on each sample. Prior to the dose recovery aliquots were bleached by the blue LEDs of the RISØ reader at room temperature, and irradiated with a dose similar to the one determined through initial trial measurements.

During the evaluation of D_e some of the aliquots were rejected mainly for the following reasons: the recycling ratio (the ratio of the sensitivity corrected OSL response to the first regeneration dose and that of an identical dose at the end of the measurement cycle) was outside 1.00±0.05, the error of D_e (mainly related to the fitting of the dose response curve) was larger than 10%, or the recuperation signal (the OSL response given for zero irradiation as a matter of previous thermal treatment) was over 5% of the natural signal. The distribution of D_e values usually had an overdispersion below 0.20, consequently, and by considering the decision procedure of (Bailey and Arnold 2006) the central age model was applied for most of the calculations, however in one case, at sample OSZ869 (σ_{OD}=0.27) the minimum age model was chosen (Galbraith et al., 1999; Galbraight and Roberts, 2012).

Fig. 2 Sampling at the exposure beneath the carbonate bench by using steel cylinders

Environmental dose rate was determined by using high resolution, low-level gamma spectrometry. Dry dose rates were calculated using the conversion factors of Adamiec and Aitken (1998). Wet dose rates were assessed on the basis of in situ water contents. Samples below the fresh water carbonate layers were close to their saturation, consequently a lower variation was attributed to their water content in the past. Samples above had a water content between 12-15 %, in their case a much larger error was assumed (Table 1). The rate of cosmic radiation was determined on the basis of burial depth following the method of Prescott and Hutton (1994).

RESULTS

Based on our preliminary investigations, we found that the quartz OSL signal is dominated by the fast component in general if compared to the decay curve of the RISØ calibration quartz (180-255 μm) (Fig. 3). Therefore, the eolian sand of Lake Kolon seems to be suitable for adequate OSL dating. Nevertheless, in case of some aliquots the presence of a later, possibly medium component can be seen. To resolve the effect of this issue on dating further analysis has to be made. In order to minimize the effect of the medium component the first 5 channels (0.8 s) were integrated and used as an OSL signal in later measurements. Background was calculated from the last 50 channels of the decay curve.

Regarding dose recovery preheat tests samples were performing the best between 200 °C and 240 °C, recovered doses were close to unity in this temperature region (Fig. 4). A full dose recovery test was not performed at this stage of the investigation. Another check on the suitability of the applied measurement protocol is the calculation of recycling ratios. Concerning this parameter values were also acceptable in the above temperature range, and most of the measured aliquots proved to be adequate for further evaluation (Fig. 4). The problem of recuperation, however, at one samples appeared to be significant during the tests (OSZ870/871). Therefore, the traditional SAR protocol was replaced by the one advised by Wintle and Murray (2006), including an elevated temperature OSL measurement (hot bleach) at the end of each regeneration cycle to decrease the effect of charge transfer (Fig. 4).

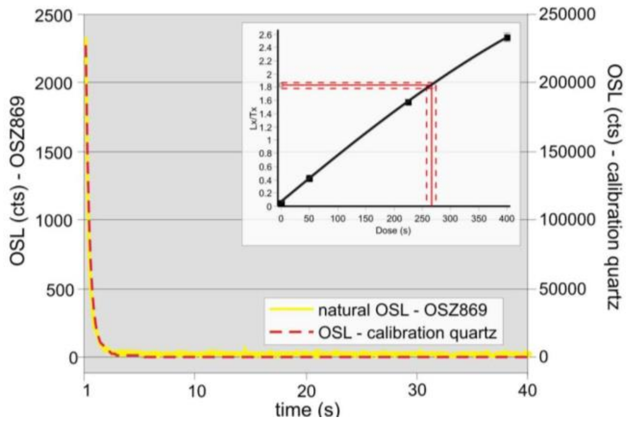

Fig. 3 Natural decay curve of an aliquot compared to that of the RISØ calibration quartz and a typical dose response curve of the same sample

With the exception of one sample (OSZ875) 24 aliquots were subjected to the SAR protocol in order to determine equivalent doses. The turnout rate of well behaving aliquots, passing all internal checks, was 70-90 % in four cases and only sample OSZ875 proved to be problematic and has to be tested further (Table 2). This means that the applied settings and protocol was proper in most of the cases.

The distribution of equivalent doses, with the exception of sample OSZ869 was unimodal and unskewed, meaning that there was an adequate exposure to sunlight during sediment transport, just as it can be expected from eolian samples (Fig 5.). Conversely, the significant skewness of OSZ869 data may imply that exposure was not adequate and the sample experienced either a short transportation distance or it was deposited by water related processes (fluvial or lacustrine).

Table 1 Sampling and radiometric data and the calculated dose rate of the samples

ID	depth (cm)	W (%)	^{238}U (ppm)	^{232}Th (ppm)	K (%)	D* (Gy/ka)
OSZ867/868	180–190	11,0±5,0	2,07±0,20	6,51±0,96	0,85±0,09	1,75±0,08
OSZ869	230	34,0±2,0	2,07±0,20	6,51±0,96	0,85±0,09	1,43±0,07
OSZ872/873	75–85	34,0±2,0	1,19±0,12	3,54±0,35	0,17±0,01	1,99±0,06
OSZ870/871	120–130	23,0±4,0	2,96±0,29	8,85±0,89	0,16±0,01	2,10±0,08
OSZ874	100	26,6±4,0	2,99±0,30	10,33±1,03	0,17±0,01	1,71±0,06
OSZ875	100	27,0±4,0	2,99±0,30	10,33±1,03	0,17±0,01	1,71±0,06

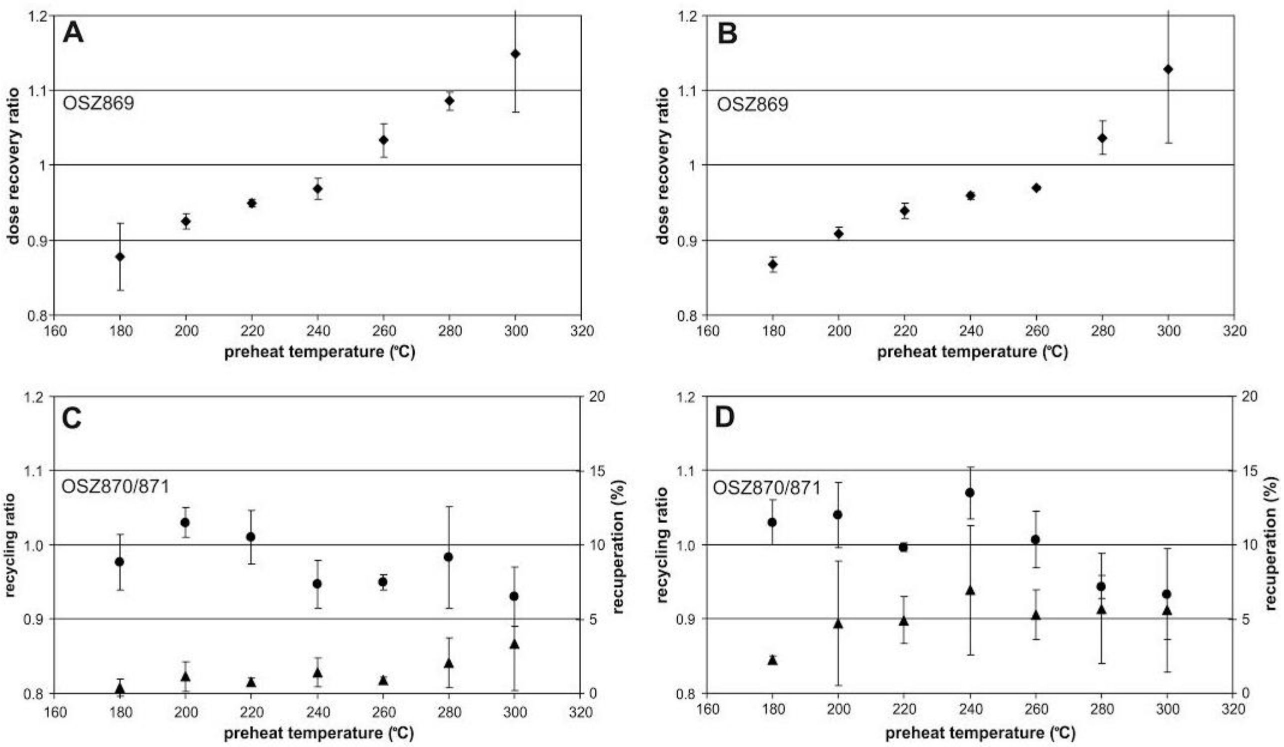

Fig. 4 Results of dose recovery preheat tests (A and B) and SAR internal checks (C and D) in case of two samples (OSZ869 and OSZ870/871)

The results of gamma spectrocopical measurements and calculated dose rates are presented in Table 1. Ages, calculated as the quotient of equivalent doses and dose rates, have a 5-10 % relative error (Table 2) and show a good stratigraphic correlation (Fig. 6).

In case of sampling point P1 the bedding of the carbonate layer was dated to the Last Glacial Maximum (23.6 ± 1.2 ka), while the cover sediments to the beginning of the Holocene (10.2 ± 0.6 ka). Consequently, the timing of lacustrine freshwater carbonate formation can be assumed for a very broad time interval.

If the stratigraphy of P1 is compared to that of P2 then the cover layer in P1 corresponds well to the bedding of carbonate in P2 (Fig. 6). Accordingly, the age of the later is also dated to the beginning of the Holocene (10.8 ± 0.7 ka). Unfortunately the cover sediments at P2 did not yield enough coarse material to carry out a successful measurement, therefore the termination of the process could not be determined. Concerning P3 the bedding of the carbonate also had a similar age (Table 2, Fig.6) as before and confirmed previous measurements. In this case the two parallel samples were dated separately, and the two dates showed a good correspondence (10.9 ± 0.4 ka and 10.4 ± 0.7 ka) (Table 2 and Fig. 6). The mean of the ages representing the beginning of the Holocene is 10.6 ka.

Table 2 Equivalent dose data and the calculated age of the samples

ID	measured/rejected (pcs)	age model	D_e (Gy)	D* (Gy/ka)	OSL age[1] (ka)
OSZ867/868	24 / 18	CAM	17,76±0,34	1,75±0,08	10,2±0,6
OSZ869	24 / 22	MAM3	33,67±0,29	1,43±0,07	23,6±1,2
OSZ872/873	–	–	–	1,99±0,06	–
OSZ870/871	48 / 40	CAM	22,82±1,09	2,10±0,08	10,8±0,7
OSZ874	24 / 17	CAM	23,59±0,12	1,71±0,06	10,9±0,4
OSZ875	18 / 8	CAM	22,49±1,47	1,71±0,06	10,4±0,7

[1] age is given by dividing D_e and D*

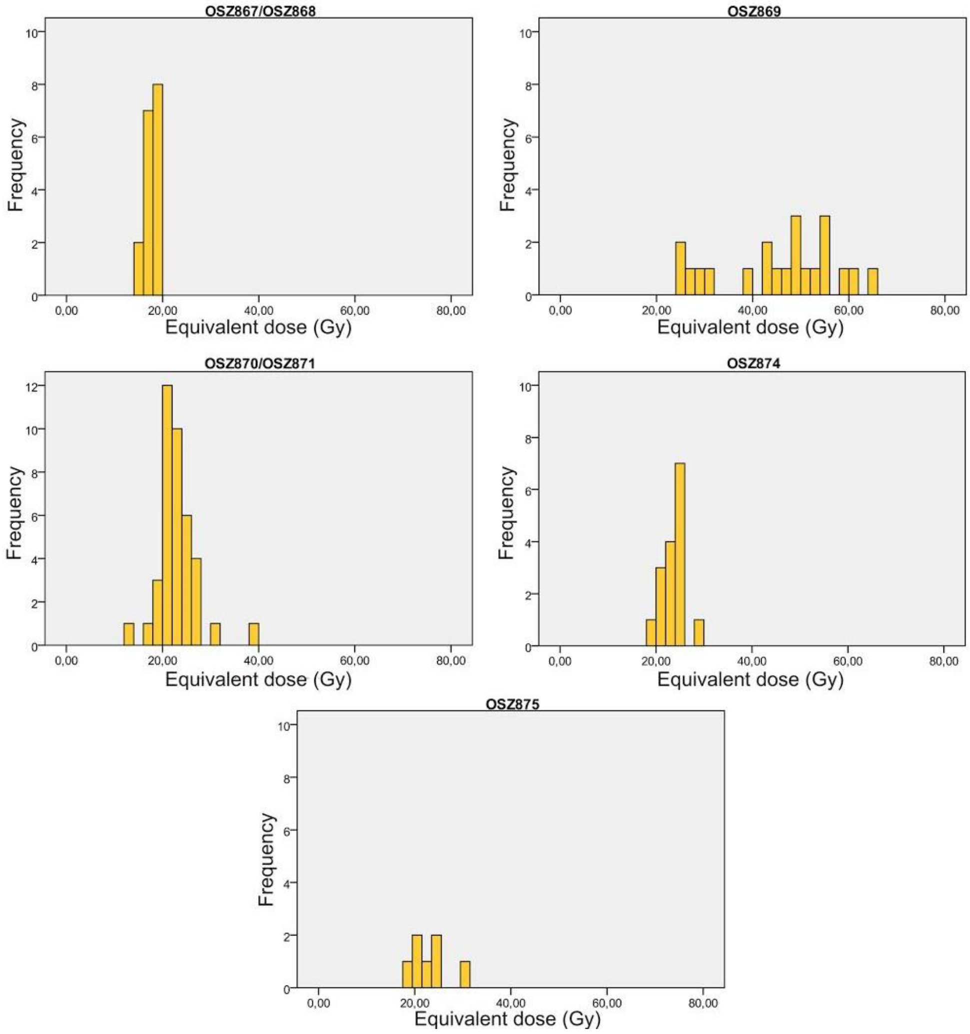

Fig. 5 The distribution of equivalent doses in terms of the measured samples

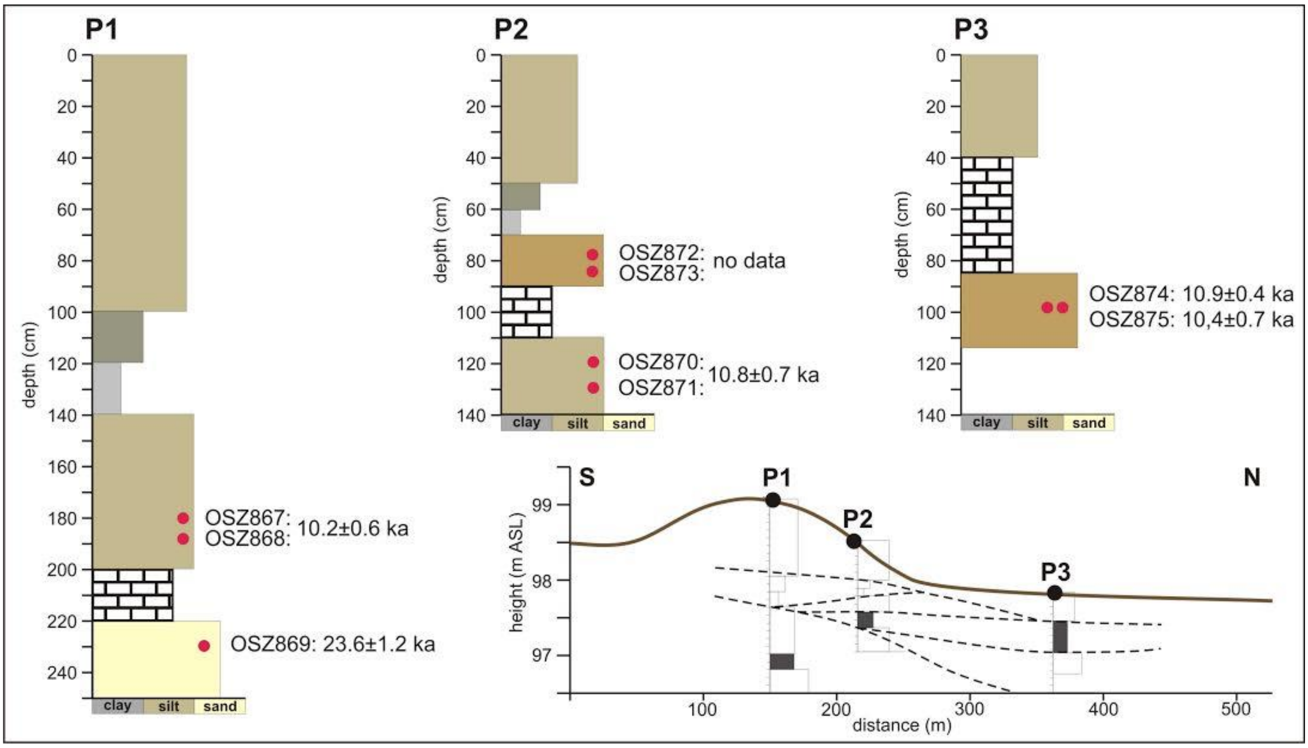

Fig. 6 The stratigraphy of the profiles and the measured OSL ages. The absolute height of freshwater carbonate layers is indicated on the inset

CONCLUSIONS

Based on various tests, the luminescence properties of the sediments originating from the Lake Kolon area are adequate for conducting a reliable dating study, only recuperation can be an issue which has to be considered especially when dating younger sediments.

The ages received at the present stage of analysis can be fitted to the radiocarbon data presented by Jenei et al. (2007) and Sümegi et al. (2011). The age of the sand layer at the base of the section is not identical to, but close to age of the earliest lacustrine layers identified by Sümegi et al. (2011) at the central part of the lake's basin. By considering the above and the dose distribution received for the material, we assume that this layer might represent the fluvial sand of the Danube.

Based on the stratigraphy and the OSL ages, it seems clear that there could be several phases of freshwater carbonate formation throughout the Late Pleistocene and Holocene. One phase is suggested to occur in the end, or after the LGM, however its precise timing needs further analysis, as there is a nearly 13 ka age difference between the layers below and above the carbonate platform. Another phase occurred after the topography had changed as a matter of blown sand movement, covering the carbonates of the first phase and forming a more pronounced topographical difference between the southern and northern part of the site. The bedding sediment of this phase is dated unambiguously to the onset of the Holocene. If the four dates corresponding to each other within their errors are averaged then a mean age of 10,6 ka is received for this event. Thus, carbonate formation occurred subsequently, though the termination of this phase could not be dated. However, based on the results of both Jenei et al. (2007) and Sümegi et al (2011) it is highly probable that there is a correspondence between the timing of carbonate formation on our site, at the centre of the Kolon Lake basin and at other sites of the DTI. Consequently, the peak of freshwater carbonate formation could be at around 10.5 ka in the region, and these deposits mark rather a relatively colder climate with variable water input, than a warm and dry environment.

Acknowledgement

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