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True and anomalous TL dates from Late Pleistocene loess-palaeosol deposits at the Kolodiiv site (East Carpathian Foreland, Ukraine)

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Twenty-five samples were selected from the Kolodiiv site (7 profiles) for total-bleach thermoluminescence dating. Only about 50% of the TL ages corresponded well to the age expected on the basis of geological interpretation. The rest of the TL dates are overestimates. The discrepancies between the TL age and the geological age of the deposits probably resulted from the presence of an admixture of poorly bleached material, of local origin, transported over a very short distance.

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INTRODUCTION

The Kolodiiv loess site is situated in the middle of the East Carpathian Foreland (Fig. 1), on the northeastern outskirts of the the Vojnylivsk Upland. The loess exposure occurs on the right bank of the Sivka River, about 15 km to the NW of the town of Halyč. The site was studied in detail by Łanczont and Boguckyj (2002), who described the following nine loess profiles within it: 1A, 1B, 2, 2A, 3, 3A, 4, 4/5 and 5. The purpose of this paper is to estimate the relation of the thermoluminescence ages obtained from these profiles with their stratigraphic interpretation based on the occurrence of palaeosols, the lithological character of the deposits, and archaeological data (Łanczont and Boguckyj, 2002). During the investigations carried out in 1998–2003, 25 samples were selected for dating in the TL laboratory of the Department of Physical Geography and Palaeogeography, Maria Curie-Skłodowska University in Lublin. It should be noted that 19 samples were taken from the Horohiv, palaeosol unit mainly from its Vistulian part, and only 6 from younger deposits. Therefore, the loess samples analysed originated mainly from the Early Vistulian, i.e. the period with climatic conditions unfavourable for accumulation of thick aeolian deposits. This fact has had a considerable effect on the thermoluminescence analysis results described in this paper.

CRITERIA OF APPLICABILITY OF THERMOLUMINESCENCE DATING METHOD

The determination of age of Quaternary deposits by the thermoluminescence (TL) method consists of calculating the time, following burial of the deposit in question by later sediments. One of the basic assumptions in thermoluminescence dating is that, at the time of deposition, the mineral grains have only a small thermoluminescence, which should be estimated and taken into consideration when determining the TL age. Most of their TL acquired earlier, i.e. in former deposits, is lost as they are exposed to sunlight during weathering and transport. However, the degree of this photobleaching can vary. A sufficiently long exposure reduces the thermoluminescence to a residual level, which then remains stable. It is commonly accepted that such a situation can take place in aeolian deposits i.e. dune sands and loesses. However, loesses often show facies differences. We can distinguish the following main facies: typical aeolian, slope (deluvial), and valley (alluvial). Facies differences in loess results from the fact that after aeolian deposition, loess silt is often displaced by processes associated with topographic relief (Maruszczak, 1991). At the Kolodiiv site, aeolian loess accumulation on the slightly inclined surface between the Sivka River terrace and the steep slope was affected by pedogenesis of different intensity, and other processes such as wash-down and soil creep (Łanczont and Boguckyj, 2002).

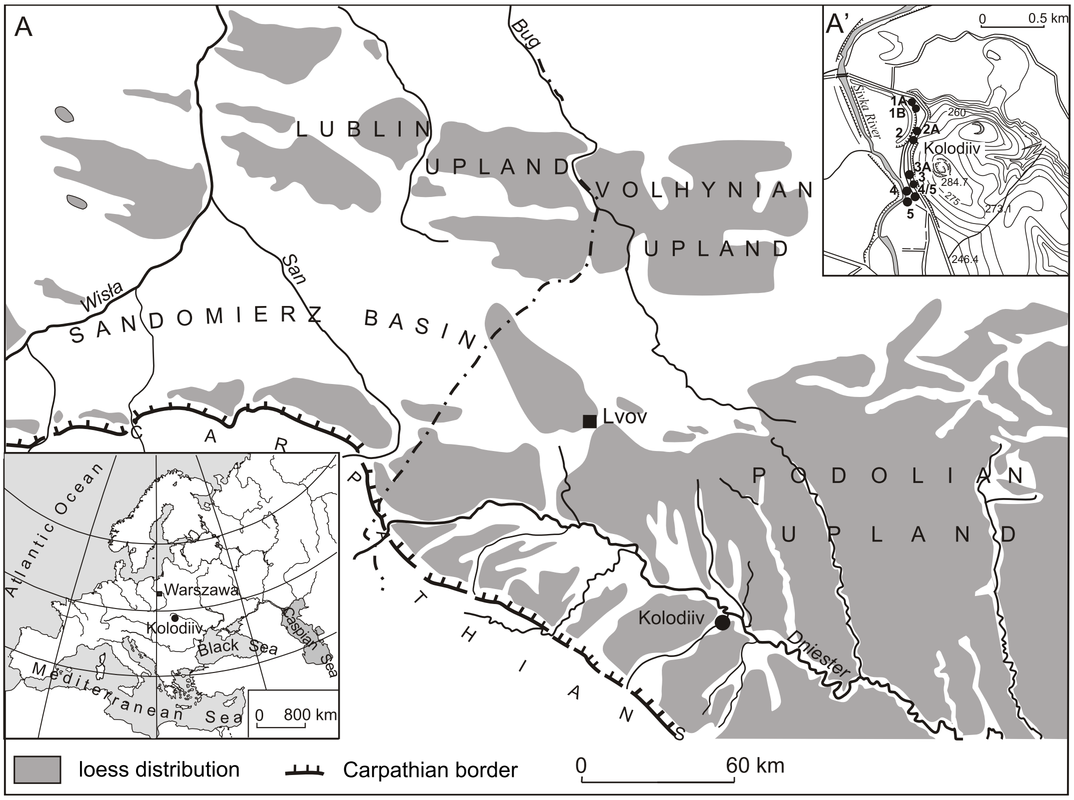

Fig. 1. A — sketch map of loess regional distribution; A' — location of profiles investigated at Kolodiiv (after Łanczont and Boguckyj, 2007)

Therefore, the effect of these processes on the TL ages obtained for the loess deposits examined will be discussed.

DATING METHOD

The TL age of the deposit equals the geological dose divided by the annual dose. The geological dose is determined as the equivalent dose (ED), i.e. the laboratory dose that produces the same TL intensity as the radiation dose absorbed by the mineral grains in natural conditions. The annual dose is defined as the effective dose of ionising radiation absorbed by the mineral grains in a unit of time (year or millennium).

The determination of ED starts from the preparation of the mineral material, i.e. the separation of a required fraction from the whole volume of a sample taken at an exposure. Loess contains 50–80% of the 2–63 μm fraction (Wintle, 1987). Therefore, grains from this range of diameters are commonly used for TL dating. In all TL measurements discussed in this paper, the 45–63 μm polymineral fraction was used. It is estimated that in loess about 95% of the TL signal comes from feldspars, and only about 5% from quartz (Singhvi and Mejdahl, 1985). That is why no separation of the mineral components from the silt fraction is usually performed. However, the polymineral fraction requires treatment with 10% HCl to remove carbonates and iron compounds, and with 30% H_2O_2 to remove organic material. After each phase of treatment, the mineral material is washed with distilled water several times.

Then, the mineral material obtained from each sample is divided into portions (6–9) in order to record several TL glow curves, i.e. from natural, bleached, and laboratory-irradiated subsamples. One subsample is left as natural. A second subsample is bleached, i.e. exposed to light, in order to determine the residual level of thermoluminescence, which should be taken into consideration to avoid overestimation of the ED. Mineral grains are exposed for 12 hours to light that simulates sunlight (e.g. from an ultraviolet lamp of *OSRAM ULTRA-VITALUX* type). Several subsamples are irradiated with use of a ^{60}Co γ source. Irradiation doses (from several to several thousands Gy) are individually selected for each sample, according to its natural TL. Then all subsamples are preheated at 160°C for 3 hours in order to obtain the maxima of glow curves at the same temperature.

The TL glow curves are recorded using the *RA'94* reader. Each 4 mg portion is put on a special platinum plate, and heated at a constant rate (10°C/sec.) up to 400°C. Heated minerals emit light of a characteristic wavelength range (Wintle, 1997). Optical filters are used in order to obtain a narrower TL signal. The measurements presented in this paper were made using a *BG-28* (380–500 nm) filter. The emitted light was recorded with a *EMI 9789 QA* photomultiplier, and then presented as a plot of TL intensity versus temperature, i.e. a glow curve.

To determine the ED, the maximum heights of all obtained glow curves should be read and plotted as thermoluminescence intensity (TL) versus irradiation dose (D). A linear or exponential function is fitted to the points obtained, and extrapolated to the X-axis. The intersection point shows the ED value. The ED was calculated with the *FIT-SIM* programme of Grün (1994) which is based on the simplex fitting procedures and analytical error calculation by Brumby (1992). A plateau test was carried out for each sample.

The annual dose is the sum of d_α, d_β, d_γ, and dc, i.e. dose rates from α, β, γ, and cosmic radiation, respectively. Dose rates d_α, d_β, d_γ were calculated from the concentration measurements of natural radionuclides occurring in a sample, with use of a *MAZAR 95* spectrometer, on the basis of data published by Aitken (1983) and Wintle (1987). The cosmic dose rate (d_c) was calculated on the basis of data published by Prescott and Hutton (1988), with regard to the depth of deposit occurrence. Corrections for deposit moisture were taken after Berger (1988).

RESULTS OF THERMOLUMINESCENCE ANALYSIS

The results of the thermoluminescence analysis are given in Table 1 and Figures 2 and 3. The particular stratigraphic units, that were TL dated are named according to the stratigraphic scheme of the Vistulian loesses and intraloess palaeosols in the Halyč Prydnistrov'ja region published by Boguckyj and Łanczont (2002).

The Upper and Middle Pleniglacial deposits (OIS 2 and 3) were TL dated in profiles 1B, 2 and 2A (6 samples). Two TL ages (46±8 and 50±8 ka) were obtained for the same sample (Lub-3354) from the Dubno 2 palaeosol (OI substage 3.3) in profile 1B. These results correspond well to geological age of the deposits examined. Three samples (Lub-3685–Lub-3687) were taken from profile 2A. One sample from the L1–l1 loess (OIS 2) was dated at 26±4 ka, and expected TL age. Two samples taken from the Dubno 1 unit were dated at 103±18 and 115±28 ka. These dates are considerably older in comparison to the ages expected on the basis of geological interpretation, probably because of the occurrence of material redeposited from nearby older strata. A similar situation was found in profile 2. Sample Lub-4012 from a silty-sandy solifluction layer overlying the upper gley horizon of the Dubno 1 palaeosol was dated at 54±7 ka, and the sample Lub-4013 from the B horizon of this palaeosol gave an age of 76±712 ka. Both results are older then expected.

The Horohiv pedocomplex (OIS 5) was sampled (19 samples) in profiles 1A, 2, 3A, and 4. It contains two sets of palaeosols. A well-developed interglacial forest lessivé palaeosol constitutes its Eemian part, which is overlain by three Early glacial interstadial palaeosols (Kolodiiv 1, Kolodiiv 2 and Kolodiiv 3) corresponding the West European warmings, i.e. Odderade, Brörup, and Amersfoort (Łanczont and Boguckyj, 2002). Three samples (Lub-3351–Lub-3353) were collected from profile 1A. The loess underlying the Kolodiiv 2 palaeosol was dated at 111±21 ka, a humus horizon of the Kolodiiv 3 palaeosol yielded 146±26 ka, and the Bt horizon of interglacial forest palaeosol gave a date of 164±30 ka. One sample (Lub-3688) was taken from a solifluction layer overlying the Kolodiiv 3 palaeosol in profile 3A; the TL age obtained is

Table 1

Results of TL dating for the Kolodiiv site

Profile depth [m]	No. lab. (Lub-)	Dose rate Dr [Gy/ka]	Equivalent Dose ED [Gy]	Age [ka]
1A (3.85)	3351	1.753	194 31	111 21
1A (4.3)	3352	1.684	250 37	148 26
1A (4.95)	3353	1.823	299 45	164 30
1B (0.2)	3354	2.444	112 16 123 17	46 8 50 8
2 (4.50)	4012	2.734 0.25	147 11	54 7
2 (5.20)	4013	2.861 0.31	218 22	76 12
2 (14.30)	4014	2.25 0.21	216 20	96 12
2 (14.60)	4015	1.899 0.17	176 21	92 14
2 (15.50)	4016	2.258 0.25	237 28	105 17
2 (16.60)	4017	2.496 0.22	301 36	121 18
2 (17.40)	4018	2.347 0.25	342 35	146 22
2 (18.50)	4019	2.76 0.26	416 52	151 24
2A (5.2)	3685	2.86	75 10	26 4
2A (10.5)	3686	3.121	320 49	103 18
2A (11.6)	3687	2.949	340 80	115 28
3A (2.1)	3688	2.373	278 73	117 32
3 (11.30)	4171	2.152 0.2	204 54	95 15
3 (11.70)	4172	2.1551 0.3	285 24	132 19
3 (13.10)	4173	2.825 0.21	462 48	164 15
3 (13.60)	4174	2.942 0.22	538 75	183 18
3 (14.00)	4175	3.559 0.32	723 124	203 24
4 (0.25–0.4)	3521	2.484	300 42	121 18
4 (1.6–1.65)	3522	3.414	500 65	146 20
4 (2.8–2.85)	3523	3.668	601 90	164 26
4 (4.1–4.2)	3524	3.753	630 83	168 25

117±32 ka. Four samples (Lub-3521–Lub-3524) were dated in profile 4 (Fig. 4). The Kolodiiv 2 palaeosol was dated at 121±18 ka, the Kolodiiv 3 palaeosol yielded 146±20 ka, a dark greenish-grey loam underlying the Kolodiiv 3 palaeosol gave 164±26 ka, and a silty loam underlying the Eemian gyttja gave a date of 168±25 ka. Five samples (Lub-4171–Lub-4175) were collected from profile 3. Loamy-sandy deposit of the Kolodiiv 1 palaeosol was dated at 95±15 ka, a loamy-sandy deposit of the Kolodiiv 2 palaeosol yielded 132±19 ka, while three samples from the Kolodiiv 3 palaeosol gave a date of 164±15, 183±18, and 203±21 ka. Six samples (Lub-4014–Lub-4019) were collected from profile 2. Two of these came from the Kolodiiv 2 palaeosol (96±12 and 92±14 ka), one from a humus horizon of the Kolodiiv 3 palaeosol (105±17 ka), and three from loamy-sandy deposits of the Eemian palaeosol (121±17, 146±12, and 151±21 ka).

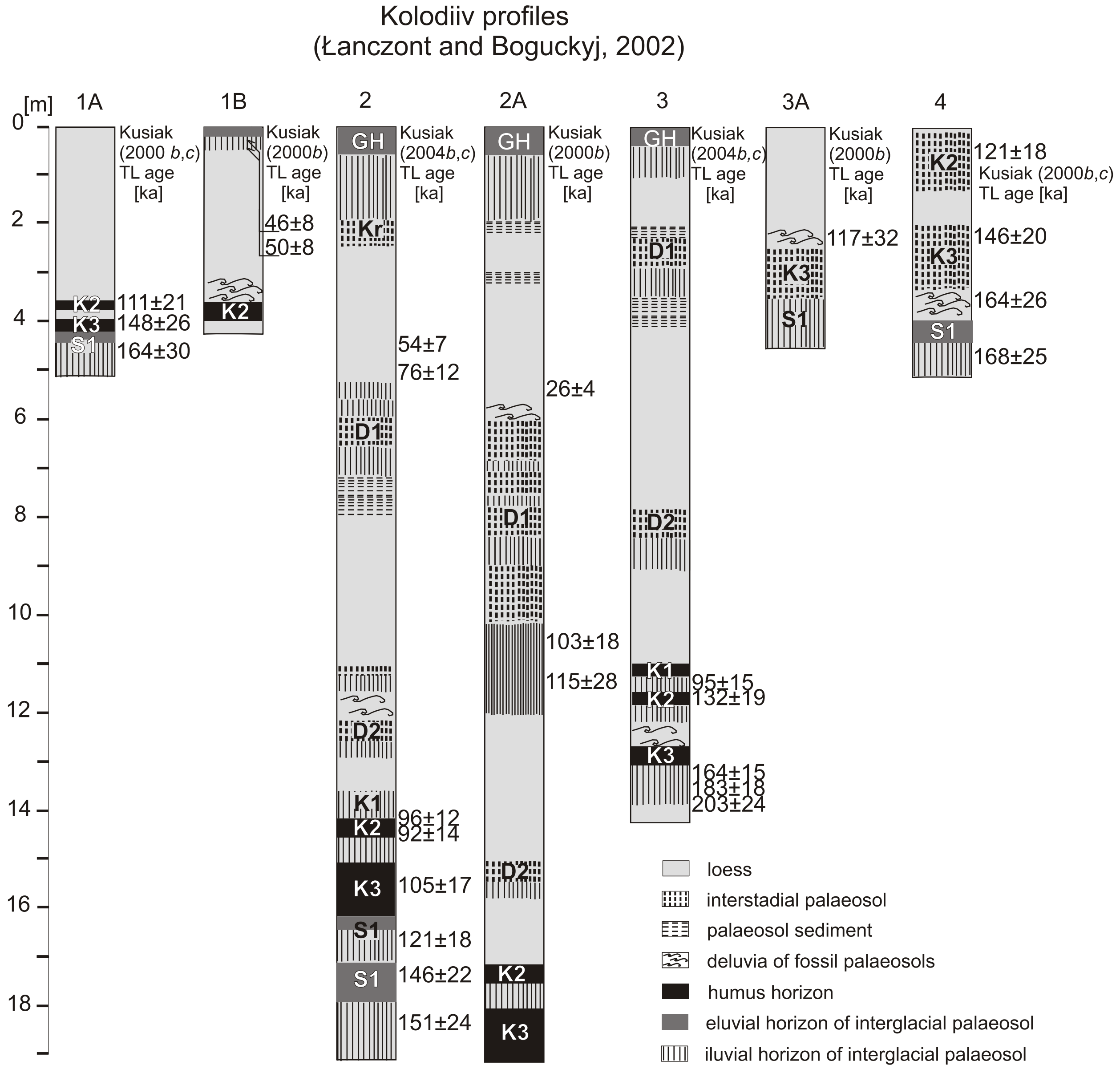

Fig. 2. Sample collection points in the profiles of the Kolodiiv site

GH — recent palaeosol; intraloess palaeosols: Kr — Krasyliv, D1 — Dubno 1, D2 — Dubno 2, K1 — Kolodiiv 1, K2 — Kolodiiv 2, K3 — Kolodiiv 3, S1 — interglacial palaeosol

The TL ages obtained for the deposits correlated with OIS 5, as do those discussed above for TL dating of the Upper and Middle Pleniglacial deposits (OIS 2 and 3), can be classified into two groups: data corresponding well to the ages expected on the basis of geological interpretation, and dates that appear too old. The first group contains TL ages of the following samples: six from profile 2 (Lub-4014–Lub-4019), Lub-3351 and Lub-3353 from profile 1A, Lub-4171 from profile 3, Lub-3688 from profile 3A, and Lub-3524 from profile 4. The remaining TL ages of eight samples seem to be considerably too old. Two of them came from the Kolodiiv 2 palaeosol (Lub-4172 from profile 3, and Lub-3521 from profile 4). The results of TL dating of six samples collected from the Kolodiiv 3 palaeosol are especially anomalous, i.e. of one sample (Lub-3352) from profile 1A, three samples (Lub-4173–Lub-4175) from profile 1A, and two samples (Lub-3522 and Lub-3523) from profile 4.

CONCLUSIONS

The author has carried out thermoluminescence dating of loess deposits from Southern Poland and northwestern Ukraine for about ten years. The results have been published, in Dolecki (1998, 2002), Łanczont *et al*. (1998), Lindner *et al*. (1999), Dolecki and Wojtanowicz (2000), Dolecki and Łanczont (2001), Harasimiuk and Jezierski (2001), Rzechowski (2001), Łanczont and Boguckyj (2002), Dolecki *et al*. (2003), Nawrocki *et al*. (2003), and other papers. A compilation of these results (Kusiak,

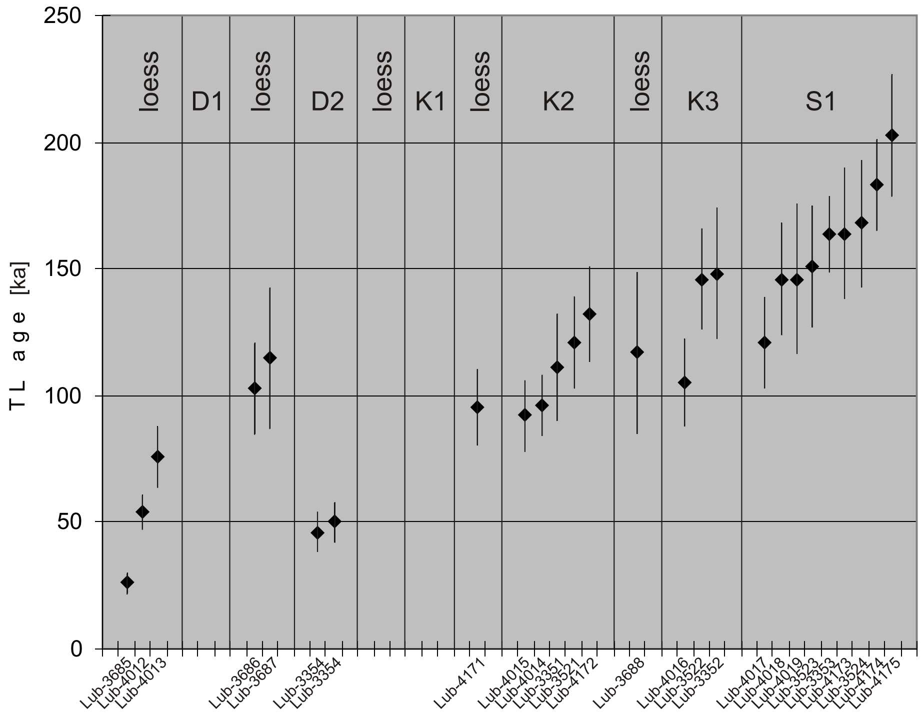

Fig. 3. TL dating results of the Vistulian and Wartanian deposits from Kolodiiv

For other explanations see Figure 2

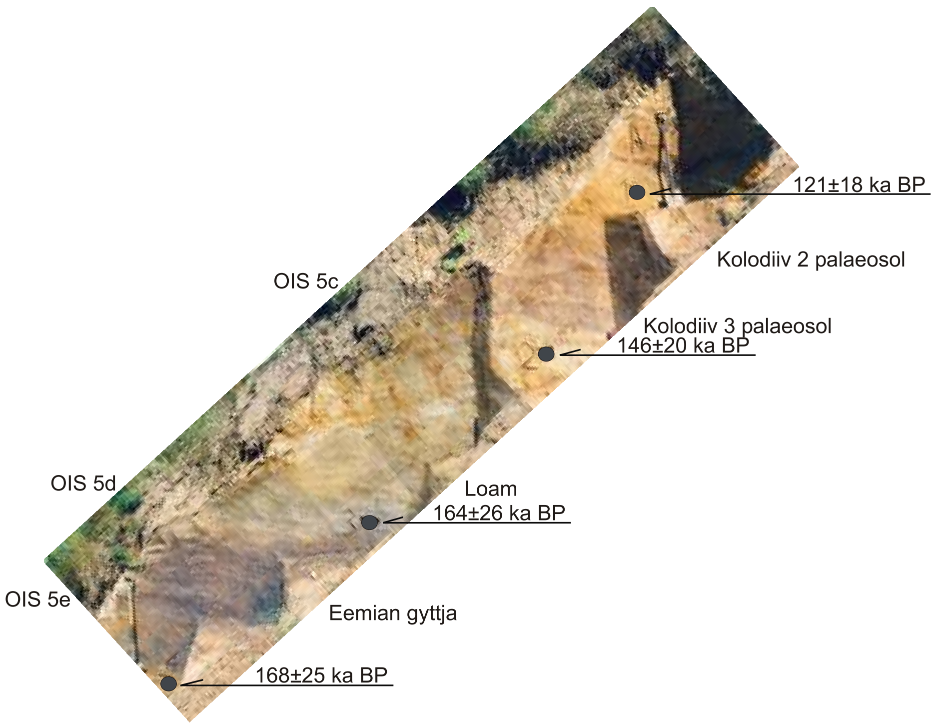

Fig 4. The Kolodiiv 4 profile

TL ages of Early Vistulian deposits

2004*a*, *b*, *c*) shows that the TL ages obtained for the last glacial cycle were mostly consistent with geological interpretation, and only some of them were overestimates with respect to the expected age of the deposits. However, the Kolodiiv site is exceptional in this respect. Only about 50% of the TL ages obtained correspond well to those expected on the basis of geological interpretation. The remaining results are too old, some of them considerably (Łanczont and Boguckyj, 2002).

The discrepancies between the TL age and geological age of the deposits in the Kolodiiv site resulted probably from the complicated nature of deposition (aeolian and slope processes), which occurred in the area examined during loess accumulation in the Upper and Middle Pleniglacial, and also in the Early Vistulian. However, anomalous ages were obtained only for some profiles from the Kolodiiv site, or from parts of them. Therefore, these phenomena, that complicate the interpretation of TL dates are only locally developed.

On the other hand, the anomalous results of TL dating of these deposits from the Kolodiiv site give additional, useful information. The field observations of Boguckyj and Łanczont, together with laboratory analyses, indicated the presence of different source areas and demonstrated complicated nature of depositional and post-depositional processes, the results of TL dating supporting such conclusions. TL ages consistent with geological ages indicate long exposure of mineral grains to sunlight, i.e. they indicate that well-bleached material underwent long-distance transported. The anomalous TL ages are associated with the occurrence of an admixture of poorly bleached material, probably of local origin, transported over short distances.

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