

Research paper

# IR-OSL dating of uranium-rich deposits from the new late Pleistocene section at the Voka site, North-Eastern Estonia

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## Abstract

This paper presents a series of results obtained from the 22 m thick deposits of the late Pleistocene section at the Voka site, NE Estonia. The section has been intensively studied during the past few years to elucidate the dynamics of the late Weichselian palaeoenvironmental changes in the Baltic region. According to the results obtained, the sediments at the Voka site were deposited in presumably freshwater sedimentary basin, which existed at least during the whole pre-Late Glacial Maximum (LGM) period of late Pleistocene (MIS 5 to 3). One of the characteristic features of the deposits is the high uranium content (up to 23 ppm) in the upper part of the section studied. This study aimed to focus on the influence of potentially unstable environmental radioactivity on dosimetric dating results due to possible disequilibrium in the U decay chain. It was found that despite the high uranium content in the deposits, the dispersion of the dates obtained is surprisingly low. At the depths with the highest uranium content, only a moderate increase of the dispersion of the ages is observed.

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## 1. Introduction

Possible secular instability of the environmental dose rate can pose a problem when using dosimetric dating methods (ESR, TL, OSL, etc.). The environmental dose rate and hence the dose absorbed by minerals during burial is mainly generated by radioactive elements in the matrix and in the minerals themselves, and by the cosmic rays. When calculating the age, it is commonly assumed that the radiation environment was constant over the period of time the sample was buried. At the same time, the disequilibrium in the radioactive decay chains seems to be quite probable due to migration of isotopes in the sedimentary matrix. Most frequently, disequilibrium occurs in the U decay chain due to the high migration ability of some of the parent isotope. The migration that occurred during burial may cause deviation of the measured environmental dose

rate from the averaged one over the long-term period of burial and, hence, the age of the deposits may be inaccurate.

In this paper, a series of results obtained from the uranium-rich deposits from the new late Pleistocene section at the Voka site, NE Estonia, is presented. The deposits studied are exposed in two neighbouring outcrops. The IR-OSL dating results obtained from these outcrops are compared to assess the extent to which the possible instability of the environmental radioactivity can affect the dosimetric dating results.

## 2. Study site

The Voka site is situated in the eastern part of the southern coast of the Gulf of Finland (Fig. 1A) where a steep cliff—the North-Estonian Clint—is interrupted by an about 2.2 km wide clint bay (Fig. 1B) filled with thick Quaternary deposits.

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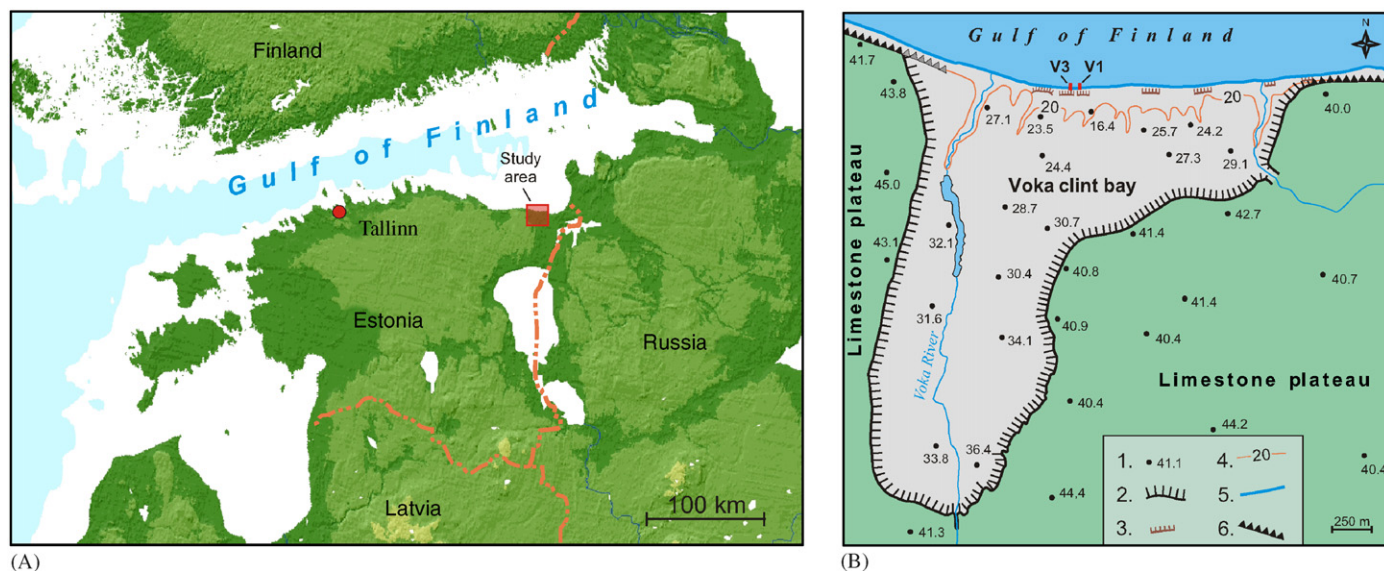


Fig. 1. Location map of the study area (A) and scheme of the clint bay with locations of the outcrops V1 and V3 (B); 1—elevations above sea level indicated in meters; 2—Clint bay boundary; 3—outcrop; 4—20-m contour line; 5—coastline; 6—Clint.

### 3. Outcrop and deposits

The deposits studied are exposed along the Gulf coast about 500 m to the east of the mouth of the Vasavere (Voka) River (see Fig. 1B) in two neighbouring outcrops V1 and V3 ( $59^{\circ}24.86'N$ ,  $27^{\circ}35.94'E$  and  $59^{\circ}24.86'N$ ,  $27^{\circ}35.88'E$ , respectively) located approximately 60 m from each other. The outcrops are separated by a ravine (Fig. 2).

The sandy to clayey sedimentary sequence comprises at least two lithostratigraphic units, A and B (Fig. 2). The boundary between these units is marked by a gravel bed at the base of unit A. Unit A is about 4 m in thickness in the eastern (V1) and about 10 m in thickness in the western (V3) section.

Lithostratigraphic unit A is characterised by alternating laminated fine sand and clay. This alternation presumably indicates the main source of the sediments: incision slopes and reworked deposits from the south of the study site. It is believed that this unit, characterised by parallel, mostly horizontal lamination, was laid down in a freshwater basin (Molodkov and Bolikhovskaya, 2005).

Unit B is represented by fine- to medium-grained sands with clayey interlayers in the eastern, and coarse-grained cross-bedded sands in the western part of the section. The maximum visible thickness of the unit is about 15 m. Most likely, the deposits of this unit were also laid down in a freshwater basin.

The deposits forming the upper part of unit A in the exposure V3 are characterised by a high content of uranium—up to 23 ppm. This relatively high value is due to the considerable amount of uranium-rich Ordovician Dictyonema argillite (black shale) (in Fig. 3A seen as very thin black layers like black book-pages stuck together).

Besides the high uranium content, deposits of unit A are characterised by the high degree of inhomogeneity due to the laminated structure of the sediments (Fig. 3B).

Taking into consideration the bedding, stratification, grain size of sediments, and other geological indications, it was widely believed to this very day that these sediments were deposited in subglacial environment at the end of the last glaciation (Raukas and Stankowski, 2005) or in an ice lake at the end of the late Pleistocene when the ice margin was located either in the Gulf of Finland or already at the South of Finland (Miidel, 2003). That is, between about 14 370 and 12 200 cal. years ago.

### 4. Luminescence analysis

#### 4.1. Sample preparation

All samples were prepared for the luminescence analysis according to standard laboratory procedures. Briefly, alkali feldspar grains in the size range of 100–200  $\mu\text{m}$  were extracted from the sediment under subdued filtered light in the laboratory by a procedure including wet sieving, heavy liquid flotation (collecting 2.54–2.58  $\text{g cm}^{-3}$  fraction), and treatment by 20–40% HCl acid to remove carbonates. The  $\alpha$ -affected surface layer of the K-feldspar grains was removed by hydrofluoric acid. The further treatment with HCl ensured removal of fluorides. Finally, the etched feldspar was sieved once more to provide 100–150  $\mu\text{m}$  grains for dating.

#### 4.2. IR-OSL measurements

The IR-OSL measurements were made with a computer-controlled Ingrid-Type SLM-1 reader using 860 nm stimulation by short 3 s laser pulses. The light beam power on

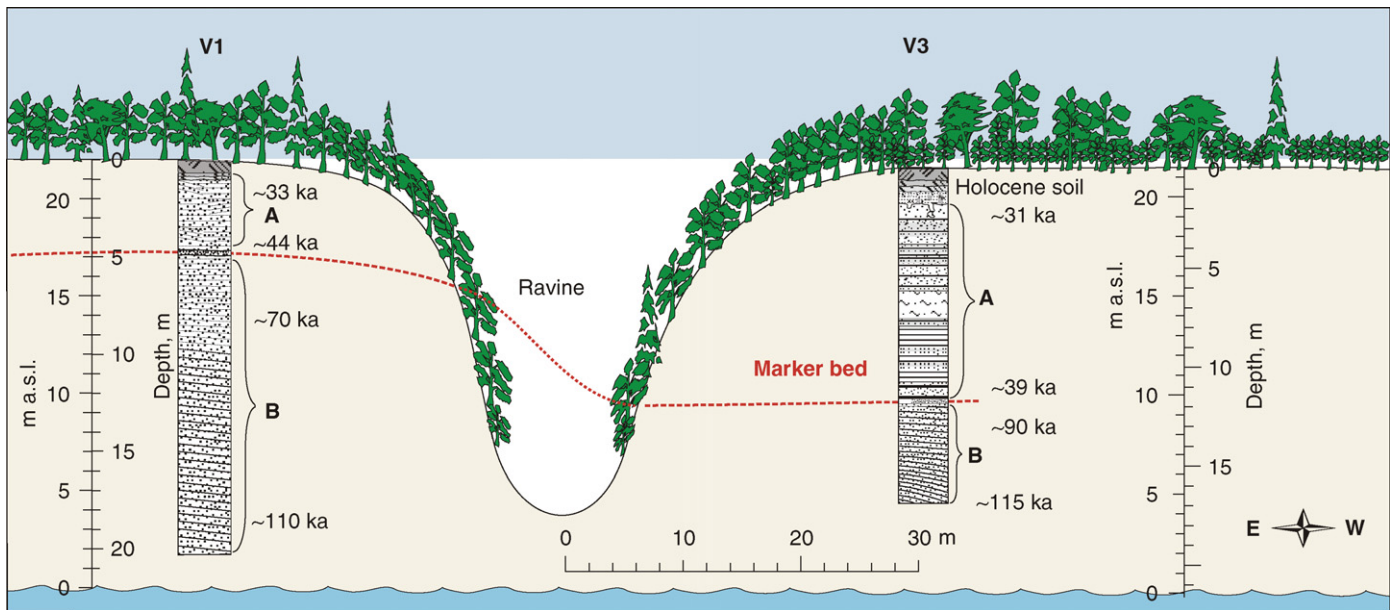


Fig. 2. Scheme of the Voka outcrops.

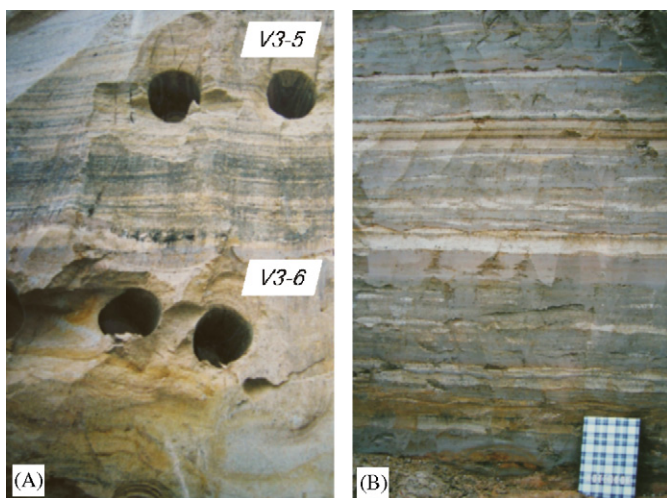


Fig. 3. Photographs showing uranium-rich thin black layers with *Dictyonema argillite* (A), and typical deposits of unit A in V3 section represented by fine- to medium-grained sands with clayey interlayers (B). Large black dots in (A) are the round holes, 75 mm in diameter, which remained after sampling for IR-OSL dating (sample V3-5 above and V3-6 below at the depths of 3.2 and 3.6 m, respectively). The notebook shown in the right lower corner of (B) measures 140 mm × 205 mm.

the aliquots was  $5 \text{ mW cm}^{-2}$ . The IR-stimulated luminescence from K-feldspar was measured in the 380–430 nm wavelength range using a combination of 3 mm SZS-22 (blue–green), 3 mm PS-11 (purple) and 2 mm FS-1 (violet) colour glass filters manufactured by the LZOS, JSC (Lytkarino Optical Glass Factory), Russian Federation. Determination of equivalent dose,  $D_e$ , was performed by extrapolating the dose–response curves to zero IR-OSL intensities using the multiple-aliquot additive-dose protocol. Additive-dose growth curves were constructed using 10–15 dose points, each consisting of measurements of 5–8

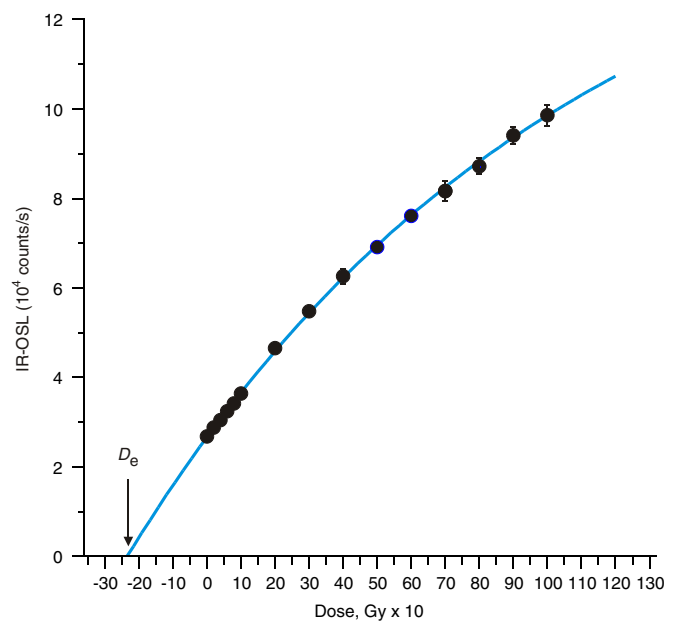


Fig. 4. Multiple-aliquot additive-dose–response curve for sample RLQG 1555-065 taken at a depth of 4.0 m from the deposits of V3 section with the highest uranium content. Each point in dose–response curve is the average from 5 aliquots. Error bars on symbols indicate standard deviation; where absent, bars fall within symbols.

separate aliquots. A typical growth curve showing the determination of the equivalent dose is given in Fig. 4. Aliquots of each sample were  $\gamma$ -irradiated using a  $^{60}\text{Co}$  source with a dose rate of  $6.5 \times 10^{-2} \text{ Gy s}^{-1}$  to a maximum dose of 1000 Gy. After irradiation, samples were kept at room temperature for at least 4 weeks to decrease the phosphorescence effects after irradiation.

It was found that the probability of tunnelling in just-irradiated samples decreased quickly and after 1-month

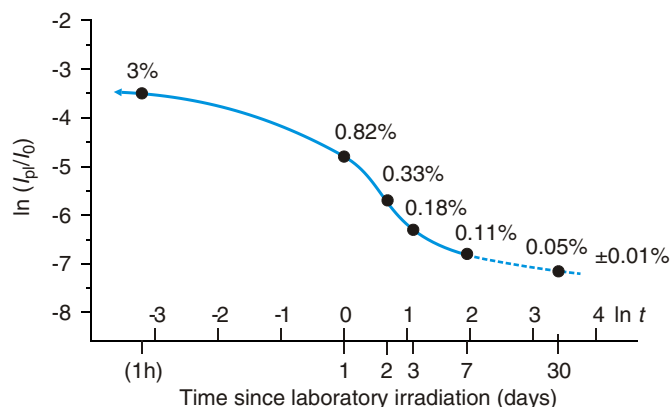


Fig. 5. Tunnelling probability as a function of time since laboratory irradiation for typical feldspar sample from the Scandinavian source region;  $I_0$  is the initial intensity at RT,  $I_{pl}$  is the plateau value in the temperature-independent section of the course of the IR-OSL intensity recorded with decrease in temperature down to LNT (for details see Vasilchenko et al., 2005). Figures at the curves are the contributions of the tunnel luminescence to the OSL signal, in percents. The last point was obtained by extrapolation of the curve to the time  $t = 30$  days. Over 1 month the tunnel luminescence comprises ca. 0.05% of the IR-OSL signal value.

storage at ambient temperature the tunnel luminescence is typically a fraction of per cent of the total IR-OSL signal (Fig. 5). This circumstance allowed to refrain from the long-term procedure of testing samples for anomalous fading, which usually is carried out by measuring feldspar samples immediately after artificial irradiation and then after storage at ambient temperature for several months.

## 5. Evaluation of annual dose

The external  $\beta$ -dose and  $\gamma$ -dose contribution to the total dose rate,  $\dot{D}$ , were estimated from the contents of natural radioactive elements,  $^{238}\text{U} + ^{235}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  in the sediments using the dose-rate conversion factors of Adamiec and Aitken (1998). For detecting and identifying naturally occurring radioactive elements in the sedimentary matrix a multichannel  $\gamma$ -ray spectrometer equipped with a 150 mm diam.  $\times$  100 mm low background sodium iodide crystal was used. Representative samples of about 1.5–2.0 kg in weight were used for the measurements. Attempts were made in the field to take all samples from the most homogeneous layers. The contribution of cosmic rays to the total dose rate was calculated using the formula of Prescott and Hutton (1994). The intensity of cosmic rays decreases with depth. In order to take into account the increase in the thickness of the deposits during burial, we used half of the present depth for calculation of cosmic ray dose as approximation to the mean burial depth over the dated period.

Water content estimates were based on what is known about the deposits. Consideration of their location and history leads us to expect that they have all been in saturation for at least 60–70% of the time since deposition.

We have therefore assumed a 65% sediment saturation. The water content used for dose rate calculation was estimated from the saturated water content, and was determined by weight loss of a sample upon drying in a drying oven at 110°C until a constant weight is reached.

The internal  $\beta$ -dose from the decay of  $^{40}\text{K}$  and  $^{87}\text{Rb}$  within K-feldspar grains (up to ca. 700  $\mu\text{Gy/a}$ ) was obtained from the concentration estimates recommended by Huntley and Baril (1997) and Huntley and Hancock (2001), respectively, and using the  $\beta$ -attenuation factors reported by Mejdahl (1979).

## 6. Dating results and discussion

Eighteen samples from unit A of the Voka section were measured with IR-OSL. Several preliminary age determinations have also been conducted on the deposits from the lower and upper parts of the underlying unit B (see Fig. 2).

The dating results obtained for unit A from the exposures V1 and V3 are presented in Table S1 (available online as Supporting material).

The deposits of about 4-m-thick unit A from the exposure V1 contain about 4–9 ppm of uranium; those from 10-m-thick unit A from V3 contain up to 23 ppm (Fig. 6), which is about a factor of 10 higher than the average natural concentration of this element in the Earth's crust (Rogers and Adams, 1969). The contribution of uranium and its daughters to the total dose rate in the uranium-rich part of unit A reaches 57%, which could lead to a wide dispersion of the ages.

The tendency of decrease of ages from the bottom towards the top of the unit is observed. Despite the extremely unfavourable dosimetric conditions (high uranium content in the deposits, high degree of inhomogeneity), the dispersion of the dates obtained is surprisingly low. At the depths with the highest uranium content, only a moderate increase of the age deviation from the best-fitting curve is observed (Fig. 7).

A complication most expected when dating geological, including water-lain, deposits is that radioactive disequilibrium can occur in the  $^{238}\text{U}$  decay chain due to the dissolution of  $^{226}\text{Ra}$  and the emanation of  $^{222}\text{Rn}$ . Besides, the high solubility of uranium ( $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{234}\text{U}$ ) isotopes can result in their isolation from daughter products and their mobilisation in groundwater (Ivanovitch, 1984). The chemistry of the leaching and the migration to the surrounding environment of uranium and its daughters (see e.g. Dyck, 1975; Langmuir, 1997) show that disequilibrium is possible in sedimentary environments. Such a disequilibrium can cause errors in dosimetric dating.

A well-known example of a source of disequilibrium is the escape of  $^{222}\text{Rn}$ —a naturally occurring radioactive gas that is produced by the decay of  $^{226}\text{Ra}$  as part of the  $^{238}\text{U}$  decay series. Because it is a gas, it is much more mobile than other radionuclides such as radium and uranium and can easily diffuse through the sediment, especially if this is

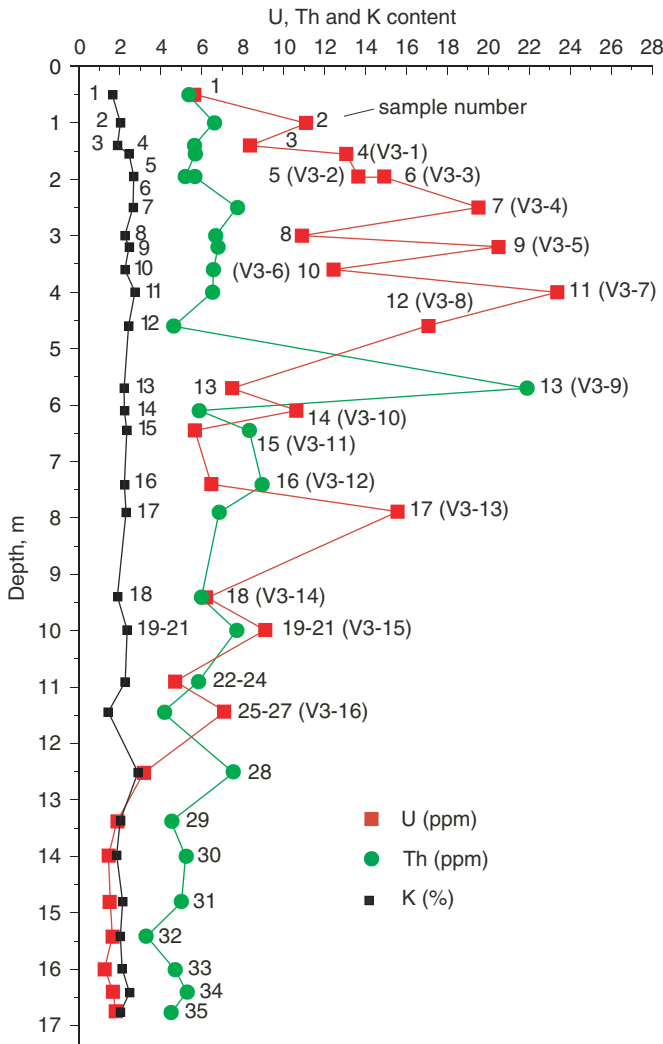


Fig. 6. Uranium, thorium and potassium contents determined by laboratory  $\gamma$ -spectrometry down the V3 section. The numbers in the brackets indicate samples dated.

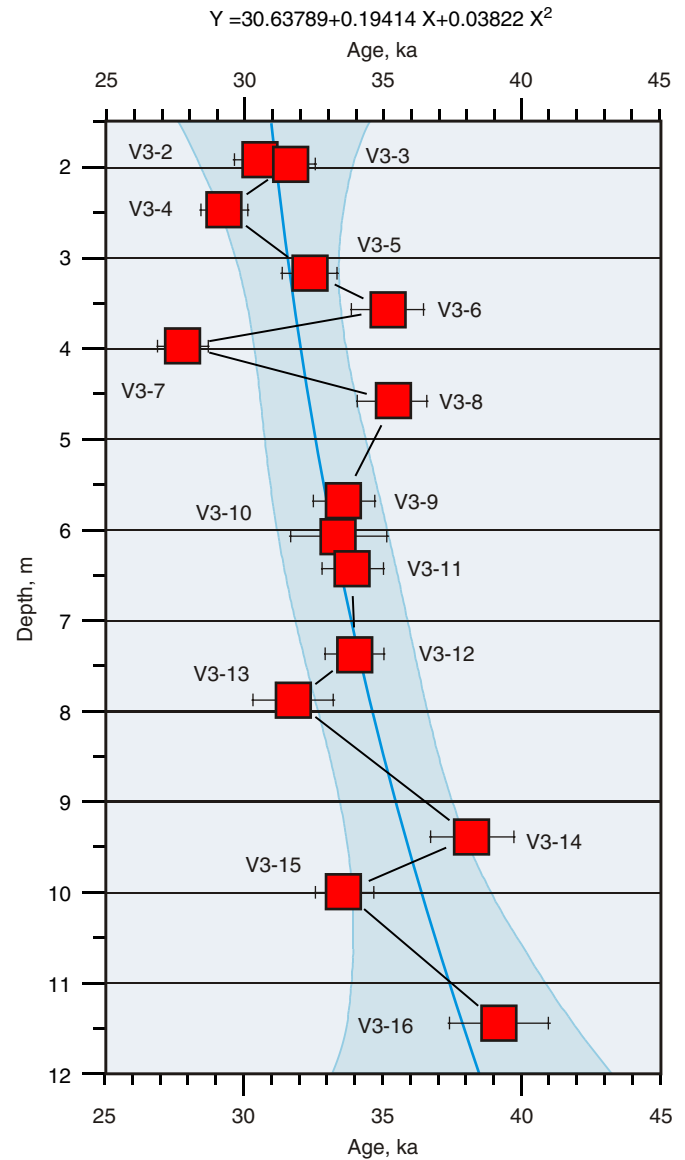


Fig. 7. IR-OSL dates (squares) from unit A of the V3 section. The best-fitting line (line is dotted in the gray version of the figure and the blue solid one in the color) for these data and 95% confidence contours (thin solid lines) with respect to this line are also shown. From the regression equation it follows that the sedimentation lasted from about 39 to 31 ka BP.

porous. The distance that a single  $^{222}\text{Rn}$  atom can cover is limited both by its mean life and the effective diffusivity. Formally, this is described by the diffusion length,  $Z_d$ , which is defined as  $Z_d = \sqrt{Dt}$ , where  $D$  is the diffusivity and  $t$  is the mean life of the radionuclide (half-life,  $T_{1/2}$ , divided by  $\ln 2$ ). The value of the diffusivity presented in the literature ranges for saturated sediments from  $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (Etioppe and Martinelli, 2002) to  $6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (Benoit et al., 1991). It means that the diffusion length for  $^{222}\text{Rn}$  over its 5.5 days mean life should be in the order of 1.0–1.7 cm. That is, that because of its relatively short 5.5-day mean life, radon typically is not transported over great distances from its source.

Another source of disequilibrium is  $^{226}\text{Ra}$  due to its solubility and relatively long half-life of 1622 years. However, the solubility of radium is generally not very high, but can increase with decreasing pH. Radium concentrations in ground water depend on the concentra-

tions of parent elements and geochemical conditions that control dissolution and sorption.

Radioactive disequilibrium in the  $^{232}\text{Th}$  decay chain is usually unimportant, as the half-lives of the daughters that tend to be mobile are relatively short. Besides, although the abundance of thorium is higher than that of uranium, the solubility of thorium is very limited and, therefore, the occurrence of its daughter elements in ground water is generally also limited.

Disequilibrium occurring in the  $^{235}\text{U}$  decay chain can also be considered insignificant, because its concentration in the natural environment tends to be very low and has no noticeable contribution to the total dose rate.

One reason why the possible post-depositional migration of uranium and its daughter radionuclides did not greatly influence the dose rate could be that one or more of the daughter products of the parent uranium have been leached out and carried into the dated matrix, approximately in the same amount.

Under favourable groundwater chemistry uranium can give stable compounds, capable of migrating over long distances. These compounds can be taken up by organic matter. Therefore, the alternative reason of relative stability of the dose rate could be the absence of organic matter in the deposits studied. Moreover, some of the

Dictyonema-rich sediments (e.g. at depths of ca 7.9 and 10.0 m, Fig. 8) are bracketed between clayey deposits and, therefore, the latter protected the surrounding sedimentary matrix from the influence of uranium-rich layers. The relatively thick layer of clayey deposits at the depths between 8.0 and 9.3 m seems to immobilise the penetration of uranium and its daughter products out of the Dictyonema-bearing sediments into the underlying sedimentary layers. At the depths between ca 1.8 and 4.7 m, where Dictyonema argillite is most abundant, the Dictyonema-rich layers alternate with the layers in which its content is visually much lower.  $\gamma$ -Spectrometric analysis of

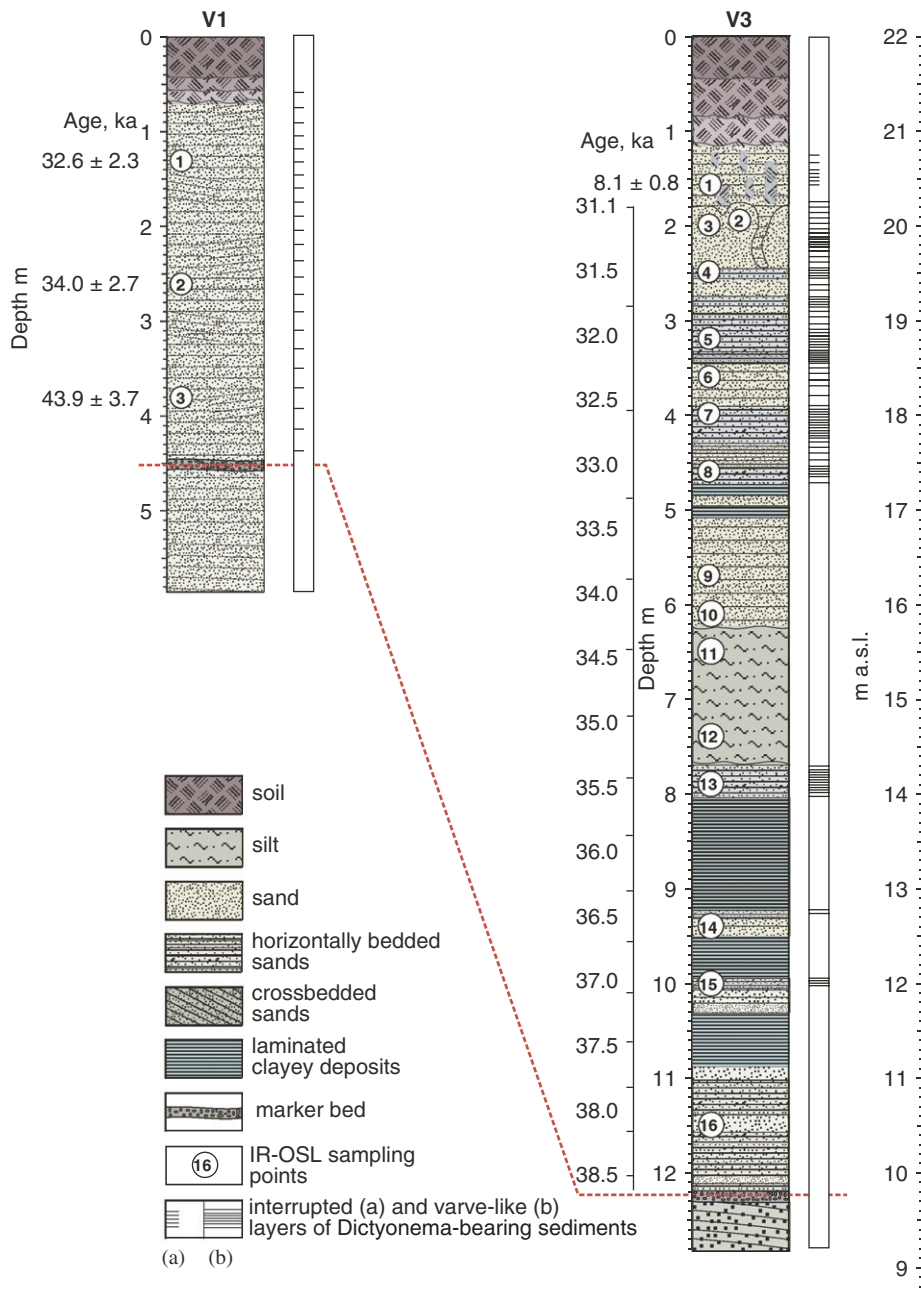


Fig. 8. Stratigraphic columns of unit A of the sections V1 and V3 at the Voka site. The numbered circles show the location of the sampling points. Shown to the right of the columns are the variations with depth of the Dictyonema argillite distribution in the deposits along the sections. Absolute time scale for unit A of the V3 section is indicated on the left.

the samples from these layers has shown that the uranium content repeats this interchange (compare e.g. U content in samples 7, 9 and 11 with those in samples 3, 8, 10, 13, Figs. 6, 8). Therefore, it seems likely that in both the Dictyonema-rich layers and beyond them, the geological dose rate remained constant over the burial period with no considerable loss or gain of uranium within the bounds of both environments. That is to say that both environments exhibit, to a certain extent, the closed system behaviour resulting in relatively insignificant dose rate change during long periods of time.

On the basis of the results obtained, the age of any part of the unit can be determined from the regression equation (see Fig. 7), and in that way the chronology of the dated part of unit A can be constructed (see Fig. 8).

In the exposure V1 where the uranium content in the unit A deposits is much lower and the deposits are considerably more homogeneous consisting basically of fine-grained sands, the same range of ages from about 44 to 33 ka was obtained. It can be interpreted as indicative of the fact that deposits of unit A in two neighbouring sections are chronostratigraphically identical, and hence were contemporaneously formed during the time predating the development of the last glaciation.

The uppermost part of the deposits in the exposure V3 is overlain by about 1.1-m-thick brownish-grey to light-brown soil resting upon ca. 0.7-m-thick layer of light-brown silt-like deposits showing signs of soil formation, densely penetrated by roots and filled krotovina-like irregular tunnels made probably by burrowing animals. These overlying deposits are most likely post-LGM in age as indicated by IR-OSL date of  $8.1 \pm 0.8$  ka for the sample taken from the lower part of the deposits at a depth of 1.6 m (see Fig. 8 and Table S1).

Single age estimates of the deposits from the underlying unit B indicate that these deposits span the period from about 110 to 70 ka (V1) and from about 115 to 90 ka (V3) (see Fig. 2). This proves the presence of the deposits of the last interglacial *s.l.* (MIS 5) here.

A gravel bed at the base of unit A marks the boundary between units A and B. Probably, this bed was formed due to erosion or a rather long sedimentation break.

The presence of older deposits (> 115 ka) is expected in the lower part of the section currently not available due to thick talus at the base of the outcrops.

## 7. Conclusions

Despite the extremely unfavourable dosimetric conditions (high uranium content in the deposits, high degree of inhomogeneity) the dispersion of the dates obtained is surprisingly low, and there is good agreement between stratigraphy and succession of the IR-OSL ages in two different sections. It demonstrates that the deviation of the calculated dose rate from the averaged one over the time of burial is less than could be expected for such complicated sedimentary sequence.

The data obtained suggest the existence of a palaeoenvironmental archive, the upper part of which (unit A) provides a record covering a time period from about 44 to 31 ka. It was also established by preliminary age estimation that the deposits of the lower part of the section (unit B) were formed during the first half of the late Pleistocene period (MIS 5 and 4). Units A and B in V3 section are most likely divided by relatively long-term interruption of sedimentation.

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## Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.quageo.2006.06.004](https://doi.org/10.1016/j.quageo.2006.06.004).

## References

- Adamiec, G., Aitken, M., 1998. Dose-rate conversion factors: update. *Ancient TL* 16, 37–50.
- Benoit, J.M., Torgersen, T., O'Donnell, J., 1991. An advection/diffusion model for  $^{222}\text{Rn}$  transport in near-shore sediments inhabited by sedentary polychaetes. *Earth and Planetary Science Letters* 105, 463–473.
- Dyck, W., 1975. Geochemistry applied to uranium exploration. *Geological Survey of Canada* 75/26, 33–47.
- Etioppe, G., Martinelli, G., 2002. Migration of carrier and trace gases in the geosphere: an overview. *Physics of the Earth and Planetary Interiors* 129, 185–204.
- Huntley, D.J., Baril, M.R., 1997. The K content of the K-feldspars being measured in optical dating or in thermoluminescence dating. *Ancient TL* 15, 11–13.
- Huntley, D.J., Hancock, R.G.V., 2001. The Rb contents of the K-feldspar grains being measured in optical dating. *Ancient TL* 19, 43–46.
- Ivanovitch, M., 1984. Application of uranium series dating to palaeoclimatic studies. *Modern Geology* 9, 249–260.
- Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice-Hall, New Jersey.
- Mejdahl, V., 1979. Thermoluminescence dating: beta-dose attenuation in quartz grains. *Archaeometry* 21, 61–73.
- Miidel, A., 2003. Stop 14. Voka outcrop. In: Raukas, A., Kukku, H. (Eds.), *Excursion Guide and Abstracts of the International Symposium on Human Impact and Geological Heritage*, pp. 33–35.

- Molodkov, A.N., Bolikhovskaya, N.S., 2005. A new Late Pleistocene site in North-Eastern Estonia: preliminary palyno- and chronostratigraphical results from the Voka section. In: International Field Symposium on Quaternary Geology and Landforming Processes, Apatity, Russia, pp. 39–41.
- Prescott, J.R., Hutton, J.T., 1994. Cosmic ray contributions to dose rates for luminescence and ESR dating: large depths and long-term variations. *Radiation Measurements* 23, 497–500.
- Raukas, A., Stankowski, W., 2005. Influence of sedimentological composition on OSL dating of glaciofluvial deposits: examples from Estonia. *Geological Quarterly* 49 (4), 463–470.
- Rogers, A.S., Adams, J.A., 1969. Uranium: abundance in common sedimentary rock. In: Wedepohl, K.H. (Ed.), *Handbook of Geochemistry*, vol. II-5. Springer, Berlin, pp. 92.K.1–92.K.5.
- Vasilchenko, V., Molodkov, A., Jaek, I., 2005. Tunnelling processes and anomalous fading in natural feldspars extracted from Quaternary deposits. *Journal of Applied Spectroscopy* 72 (2), 218–223.