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Research paper

Cross-check of the dating results obtained by ESR and IR-OSL methods: Implication for the Pleistocene palaeoenvironmental reconstructions

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A B S T R A C T

The consistency of the dating results obtained by different methods, both absolute and relative, is investigated. The main absolute methods referred to in this article are the mollusc-based electron spin resonance (ESR) and feldspar-based infrared optically-stimulated luminescence (IR-OSL) dating methods used in the Research Laboratory for Quaternary Geochronology, Tallinn University of Technology. It was shown that the parallel comparative dating by these two methods yield, essentially, consistent results. U–Th age determinations were performed in some cases for better understanding of the uranium behaviour in the shells during their burial history. ESR and U–Th dating results obtained on one and the same shell-type, both marine and land snails, coincide well in the case if shells behaved as a close system during their burial history. It is also shown that the numerical dating results obtained on warm and cold climate-related deposits, correlate well with the corresponding palaeoclimate signals derived from continuous records of the climate and environmental evolution, constructed on the base of the most common of the relative dating methods used in Quaternary studies. Based on good consistency of the results obtained by all methods used in the present comparative study, we conclude that there is a good potential to improve our understanding of the middle to late Pleistocene palaeoenvironmental evolution in Northern Eurasia, with a special focus on the climatically highly sensitive Eurasian Arctic palaeo-shelf area.

1. Introduction

Accurate and precise estimation of sediment ages is, undoubtedly, very important for geological and archaeological studies. Besides the confidence in the theoretical validity of the dating methods, the term of 'highly desirable' is to have practical confirmation that methods and techniques used provide accurate and reliable results in determining the age of geological events and materials, as well as archaeological artefacts and culture-bearing deposits. The comparison of results of different dating methods applied to samples of various materials taken from the same sampling point can be regarded as one of the best ways for the verification of their applicability and suitability. Unfortunately, it is usually quite difficult to meet these conditions in practice, especially, beyond the radiocarbon dating range.

Another, additional way to verify whether or not our dating methods are reliable, is to compare the numerical dating results obtained on warm and cold climate-related deposits with a continuous record of the climate and environmental evolution constructed on the basis of the most common relative dating methods used by Quaternary geologists (lithostratigraphy, biostratigraphy, oxygen isotope-based stratigraphy, etc.). These methods allow the ordering of physical processes occurring in nature. Once such a record of climate and environmental events is temporally ordered, the succession of identified events can be compared with the numerically dated sequence of the events.

In the present paper, we report a number of comparative results obtained using both the numerical and relative dating methods. The results were obtained in the following ways: (1) by seven parallel ESR and IR-OSL datings on shells and feldspar grains, respectively, taken from the same enclosing sediment sample; (2) by parallel ESR, IR-OSL and OSA (optically-stimulated afterglow, Jaek et al., 2003) dating on the same enclosing sediment sample using mollusc shells, feldspar and quartz grains, respectively; (3) by ESR closed-system (ESR-CS), ESR open-system (ESR-OS) and U–Th dating on the same five mollusc shells of both marine and terrestrial (land snails) origin; (4) by parallel ESR and ^{14}C dating on the same mollusc shells; (5) by numerous parallel ESR datings on shells of different mollusc species; (6) by parallel ESR datings of terrestrial shells (Molodkov, 1996a, 2001), tooth enamel (Blackwell et al.,

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2005) and palynological analysis of the inclosing sediments from a Lower Palaeolithic cave-site in the Northern Caucasus (Doronichev et al., 2007); (7) by comparison of warm and cold climate signals derived from our ESR palaeoclimatic record with those of the climatic signals derived from the long (Marine Isotope Stage (MIS) 21 to MIS 1) continuous terrestrial records (Molodkov and Bolikhovskaya, 2010); (8) by comparison of our IR-OSL dated fine-resolution late Pleistocene pollen record (Bolikhovskaya and Molodkov, 2007) with $\delta^{18}O$ variations in the NGRIP ice-core (Andersen et al., 2006).

The results obtained in this study exemplify the potential of both combined and independent use of palaeodosimetric dating methods applied to two different minerals – feldspar and biogenic carbonate – to chronologically organize the sequence of the middle to late Pleistocene palaeoenvironmental events.

2. Study area and sampling sites

Samples used for cross-checking and comparison were collected from diverse temporal (latter part of early up to late Pleistocene), geographical (from Antarctica to High Arctic) and natural environments (Fig. 1). The overwhelming majority of mollusc-based ESR and feldspar-based IR-OSL dating results are from climatically highly sensitive Eurasian Arctic palaeo-shelf area (Molodkov and Bolikhovskaya, 2010). The most comprehensive and continuous terrestrial records of climatic changes spanning up to eight last glacial/interglacial cycles, i.e. from MIS 21 to MIS 1, are derived from the famous reference sections — Arapovichi, Likhvin, Otkaznoe, Strelitsa — located in glacial, periglacial, and extraglacial zones of the East European Plain (Bolikhovskaya, 1995). A unique opportunity to realize fully the potential of the synergetic approach based on a joint and detailed palynological and IR-OSL geochronological investigation of one and the same sedimentary sequence appeared in the mid-2000s, with the discovery of a thick well-exposed continuous late Pleistocene section on the south-eastern coast of the Gulf of Finland in the vicinity of the Voka village (Molodkov et al., 2007a). This section seems to be, now, one of the most complete and comprehensively studied sequences of this age in the Baltic region.

3. Methods

Results of the following methods were most widely used for intercomparison:

1) Mollusc-based ESR dating method of two modifications: a) ESR closed-system (ESR-CS) and b) ESR open-system (ESR-OS) methods (Molodkov, 1988).
2) Alkali feldspar-based IR-OSL dating method;
3) Palynological analyses by N.S. Bolikhovskaya who contributed greatly to the terrestrial proxy climate record of the East European Plain (Bolikhovskaya, 1995).

In addition, U–Th age determinations were also performed for better understanding of the uranium behaviour in the shells during their burial history. Necessary data for both ESR-OS and U–Th age determinations were obtained by ALS Scandinavia (Sweden) from the ICP-SFMS analysis of mollusc shell samples for ^{238}U, ^{234}U and ^{230}Th.

All ESR, IR-OSL, OSA and ICP-SFMS U–Th age determinations were carried out at the Research Laboratory for Quaternary Geochronology (RLQG), Institute of Geology, Tallinn University of Technology. An overview of the ESR dating procedure used in RLQG is presented in Molodkov et al. (1998), and of IR-OSL is presented in Molodkov and Bitinas (2006).

The ESR palaeoclimatic record is used in the present study for spatially and temporally large-scale intercomparisons with climatic signals derived from different geological archives. The record is mostly based on the chronostratigraphy of mollusc-bearing climate-controlled marine deposits along the continental margin

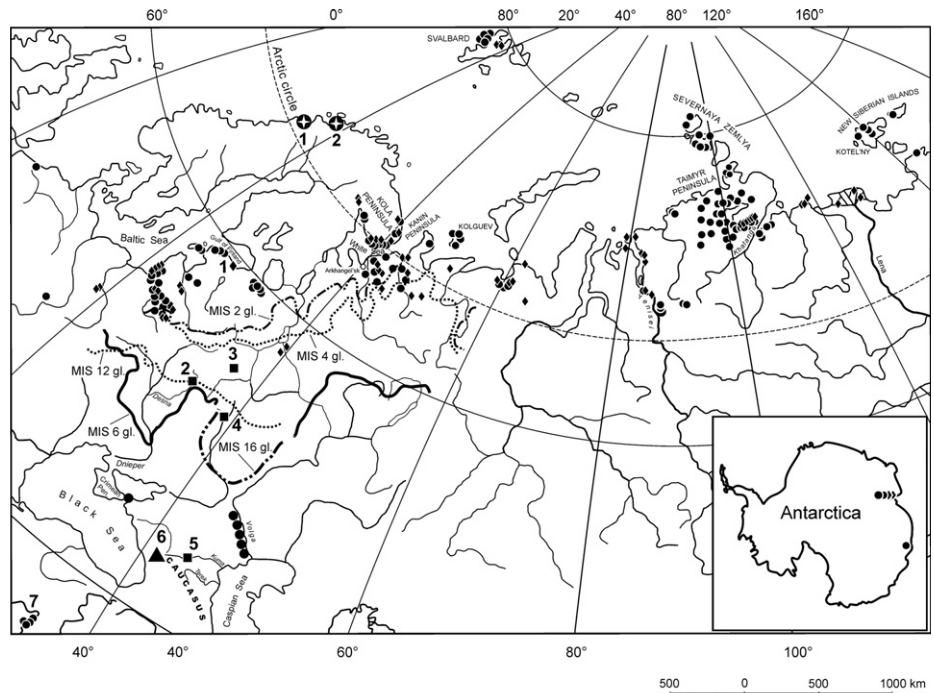

Fig. 1. Maps showing localities of sites mentioned in the text (1 – Voka, 2 – Arapovichi, 3 – Likhvin, 4 – Strelitsa, 5 – Otkaznoe, 6 – Triangular Cave, 7 – Hatay) and sites dated by ESR (circles) and IR-OSL (diamonds). The stars indicate localities of two cave sites (1 – Okshola, 2 – Stordalsgrotta) in northern Norway investigated by Lauritzen (1995). Limits of the main middle and late Pleistocene glaciations on the East European Plain (MIS 16–2 gl.) are after E. Zarrina (1991).

of Northern Eurasia. They were ESR dated to produce an independent mollusc-based chronology for multiple periods, characterized by world-wide warming, ice cap meltings, global sea level rise causing marine transgressions during which large epicontinental basins occupied vast areas of the Northern Eurasia coast (see, e.g., Molodkov and Bolikhovskaya, 2009, Fig. 2). Clusters of ESR dates in the distribution of ages of mollusc shells collected from palaeo-shelf sediments revealed a series of intervals correlative with marine transgressions. Intervals lacking ESR dates (ESR dating hiatuses) may be, in turn, interpreted as indicating relatively cold climatic conditions or the onset of glaciations in the Northern Hemisphere, accompanied by sea regressions, climate deterioration, and changes in the environments on the continent (Molodkov and Bolikhovskaya, 2010).

The ESR-based proxy record of the climate and sea level changes over the past 900,000 years has been derived from more than 400 Quaternary shell fossils, collected and dated between 1985 and 2012, in the frame of a number of international research projects. Most of them come from the palaeo-shelf deposits of the Eurasian continental margin, from the Kola Peninsula in the west to the New Siberian Islands in the east (see Molodkov and Bolikhovskaya, 2010 and references therein). Some dating results on freshwater mollusc shell samples from interglacial lacustrine deposits and terrestrial mollusc (land snail) fossils, from a Lower Palaeolithic culture-bearing deposit, have also been used.

4. Results and discussion

Intercomparison of the results obtained by different numerical dating methods are summarized in Tables 1–4 and Tables S1–S3.

Table 1
Mollusc-based ESR, feldspar-based IR-OSL and quartz-based OSA cross-checking results. Sampling location: Nos. 1, 5, 6 – Kola Peninsula, Nos. 2, 3, 4, 7, 8 – Kara Sea coastal area.

No.	Sample No. (ESR/IR-OSL/OSA)	ESR age (ka)	IR-OSL age (ka)	OSA age (ka)
1	RLQG 310-042A–D/1405-031	103.0 ± 4.2[a]	104.0 ± 8.3[a]	–
2	RLQG 317-042/1608-124	90.3 ± 10.9[b]	88.2 ± 5.4[b]	–
3	RLQG 318-042/1478-103	107.6 ± 12.4[b]	109.8 ± 6.9[b]	–
4	RLQG 319-042/1477-103	72.0 ± 4.8[b]	74.7 ± 8.3[b]	–
5	RLQG 396-039/1861-039	73.0 ± 7.5[c]	71.9 ± 8.2[c]	–
6	RLQG 400-039A–B/1862-039	73.2 ± 4.0[c]	74.4 ± 6.8[c]	–
7	RLQG –/2042-081/2042-012	–	71.1 ± 5.5[d]	70.1 ± 14.3[e]
8	RLQG 449-061A–D/ 2043-081/2043-012	74.6 ± 3.1[d]	71.9 ± 5.6[d]	71.3 ± 17.3[e]

[a] Molodkov and Yevzerov, 2004.
[b] Zarkhidze et al., 2010.
[c] Molodkov and Bolikhovskaya, 2010.
[d] Gusev and Molodkov (in press).
[e] Data presented for the first time in this paper.

Comparison of mollusc-based ESR palaeoclimatic record with the terrestrial warm and cold climate-related signals is shown in Figs. 2–4.

The results of parallel ESR, IR-OSL and OSA dating on shells, feldspar and quartz, respectively, taken from the same enclosing sediment samples, are shown in Table 1. This parallel dating by different methods, using various minerals — feldspar, quartz and biogenic carbonate — enables direct cross-checking between different palaeodosimetric dating methods, a method that is relatively rare in Quaternary geochronology. It is noteworthy that all of these datings, except RLQG 310-042A-D/1405-031, 2042-081/2042-

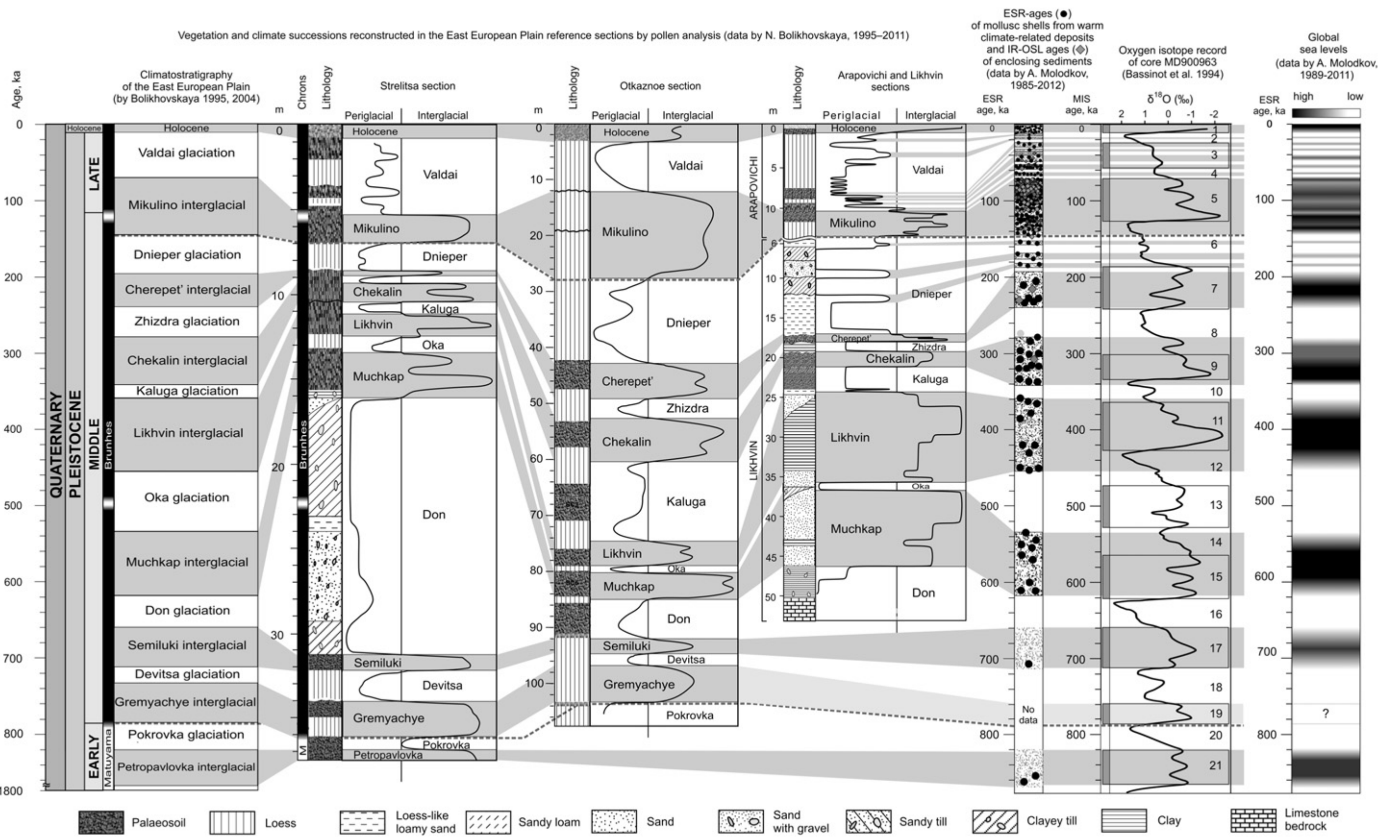

Fig. 2. Correlation of warm and cold climate-related signals from different palaeoclimatic records. Most of the ESR ages (ESR clusters) come from the climatically highly sensitive Eurasian Arctic palaeo-shelf area, IR-OSL ages – from the palynologically characterized interglacial and inter-till deposits of Northern Eurasia (updated from Molodkov and Bolikhovskaya, 2010).

Table 2
Comparison results between ESR and U–Th methods on marine and terrestrial (land snails) mollusc shells collected from deposits in the Hatay coastal region of south-central Turkey (Doğan et al., in press). ESR-CS - samples are dated by ESR closed-system method; ESR-OS - samples are dated by ESR open-system method; U–Th - samples are dated by $^{230}Th/^{234}U$ method; U_{in-m} is the measured uranium content in the shells; U_{in-av} is the time-averaged U content in the shells; U, Th, K are the uranium, thorium and potassium content in sediments as determined from laboratory gamma-ray spectrometry.

No.	Sample No.	Mollusc species	ESR-CS age (ka)	ESR-OS age (ka)	U–Th age (ka)	U_{in-m}(ppm)	U_{in-av}(ppm)	U (ppm)	Th (ppm)	K (ppm)
1	RLQG 418-090	*Spisula (S.) subtruncata triangula*	58.6 ± 4.7	56.0 ± 4.5	55.9 ± 3.2	3.68	3.87	0.67	0.07	0.17
2	RLQG 419-090	*Helix (H.) pomatia*	70.6 ± 6.4	70.6 ± 6.4	71.0 ± 2.8	0.19	0.19	1.51	0.13	0.09
3	RLQG 421-090	*Spisula (S.) subtruncata triangula*	67.1 ± 6.3	69.0 ± 6.5	65.2 ± 3.4	5.07	4.86	0.28	0.00	0.08
4	RLQG 422-090A	*Luria lurida*	46.4 ± 5.4	73.5 ± 8.8	5.6 ± 0.4	2.74	0.28	1.10	1.65	0.43
5	RLQG 422-090B	*Mytilaster lineatus*	72.5 ± 6.1	72.5 ± 6.1	77.2 ± 3.6	0.24	0.21	1.10	1.65	0.43

012 and 449-061A–D/2043-081/2043-012), were performed blindly, without previous knowledge of the counterpart dating results. In the latter case, shell samples of four different mollusc species were specially requested to perform intercomparison of the results, using different dating methods and minerals, to be sure that results obtained on a critical reference section located in the lower Yenisei River area, western Siberian Arctic, are reliable. Taken as a whole, results shown in the table demonstrate both a remarkable concordance and no evidence of noticeable athermal emptying (anomalous fading) of the feldspar dosimetric traps, neither on laboratory nor on geological time scales. The latter issue was discussed in detail by Jaek et al. (2007a,b, 2008, 2010), Molodkov et al. (2007b) and Vasilchenko et al. (2005).

Quite interesting results were obtained when dating the same shells by two independent methods, based on different physical principles — U–Th and ESR. The ESR method was used in two modifications: ESR closed-system (ESR-CS) and ESR open-system (ESR-OS) methods (Table 2). It should be noted that the conventional ESR-CS age was determined using measured ^{238}U content in the shell, whereas, ESR-OS age was determined using immobile radiogenic ^{230}Th content in it. In the latter method, according to an early work (Molodkov, 1988), the present-day ^{230}Th activity in the shell is used as an indicator of time-averaged U content in the shell, U_{in-av}. Thorium is geochemically immobile. Therefore, radiogenic ^{230}Th is, usually, permanently fixed in the shell and its residing within the shell may meet the closed-system requirements. In view hereof, the link ^{234}U–^{230}Th in the uranium decay chain may be considered as a low-pass filter ‘smoothing’ the ^{230}Th activity fluctuations in the shell after possible changes of U content value in it during its buried state, allowing the calculation of a value of time-averaged U content in the shell from the measured ^{230}Th activity.

The first three shell samples of different mollusc species shown in Table 2, (RLQG 418-, 419- and 421-090), were collected from different sections. The calculated time-averaged U content in these shells are similar to measured values of U, indicating closed-system behaviour of these shells throughout they burial histories. Dating of the shells by three methods had resulted in similar ages for two shells (RLQG 418- and 421-090) and equal ages for the shell RLQG 419-090 (70.6, 70.6 and 71.0 ka) for which measured and calculated time-averaged U contents turned out to be also equal (0.19 and 0.19 ppm, respectively).

The next two shell samples of different mollusc species (RLQG 422-090A and 422-090B) were collected from the same enclosing sediment sample. The great difference (one order of magnitude) between measured (2.74 ppm) and calculated time-averaged U content (0.28 ppm) in one of the shells (RLQG 422-090A) clearly indicates open-system behaviour of the shell: all three age determinations (by ESR-CS, ESR-OS and U–Th) are different (46.4, 73.5 and 5.6 ka, respectively). It can be concluded from these results that recent U uptake, resulting in younger ESR-CS and U–Th ages, occurred for this shell. It is highly surprising, however, that another shell (RLQG 422-090B), taken from the same enclosing sediment sample, definitely demonstrates a closed-system behaviour. The near-equality of the ESR-OS ages of these two shells (73.5 and 72.5 ka, respectively) as well as the similarity of the ESR and U–Th ages of the second shell (RLQG 422-090B, 72.5 and 77.2 ka, respectively) clearly confirms these observations.

Table 3
Some comparing results between ESR dating of different species of mollusc shells taken from the same sampling point or horizon. Six land snail shell samples collected at Treugol'naya (English Triangular) Cave (Northern Caucasus) were taken at the same stratigraphic level (layer 7a) from three different samples of enclosing sediments indicated by Roman numerals I, II and III. Samples marked with asterisk (*) are collected from the same sedimentary horizon at different depths indicated (in m) after slash mark. U_{in-m} is the measured uranium content in the shells. Sampling location: Nos. 1 to 6 – Treugolnaya Cave; 7, 8 – Severnaya Zemlya; 9 to 18 – Kola Peninsula; 19 to 23 – Taimyr Peninsula; 24 to 27 – lower Yenisei River area.

No.	Sample no. Lab. code: RLQG	Mollusc species/sampling depth within the same horizon (m)	ESR age (ka)	U_{in-m} (ppm)
1	161-062-I	*Chondrula tridens* (Müll.)	570.0 ± 54.0	0.51
2	162-062-II	*Monacha caucasicala* (Lindh.)	600.0 ± 46.0	0.43
3	163-062-I	*M. caucasicala* (Lindh.)	610.0 ± 54.0	0.38
4	164-062-II	*M. caucasicala* (Lindh.)	545.0 ± 41.0	0.42
5	166-062-II	*C. tridens* (Müll.)	565.0 ± 45.0	0.31
6	167-062-III	*M. caucasicala* (Lindh.)	610.0 ± 51.0	0.36
7	327-103A	*Mya truncata*	183.7 ± 14.5	0.64
8	327-103B	*Hiatella arctica*	183.3 ± 14.3	0.85
9	362-057A	*Arctica islandica*	61.6 ± 4.8	2.90
10	362-057B	*Astarte elliptica*	61.1 ± 4.8	3.70
11	362-057C	Unidentified fragments	66.0 ± 5.2	3.20
12	395-039A	*A. islandica*	134.5 ± 9.5	0.30
13	395-039B	*A. elliptica*	137.0 ± 9.6	0.41
14	400-039A	*H. arctica*	74.0 ± 5.2	1.70
15	400-039B	*A. islandica*	72.0 ± 6.1	1.24
16	407-039*	Unidentified fragments/12.8	316.0 ± 23.6	0.32
17	404-039*	Unidentified fragments/13.5	319.0 ± 22.7	0.35
18	406-039*	Unidentified fragments/18.6	319.0 ± 38.5	0.30
19	442-061*	*Astarte borealis*/2.0	228.0 ± 16.0	0.10
20	443-061*	*H. arctica*/3.8	232.0 ± 19.1	0.65
21	446-061*	*Portlandia arctica*/0.6	100.5 ± 12.0	0.16
22	445-061*	*P. arctica*/1.1	101.0 ± 8.7	0.14
23	444-061*	*P. arctica*/4.6	104.5 ± 8.9	0.22
24	449-061A	*A. islandica*	76.2 ± 6.0	3.85
25	449-061B	*A. borealis*	79.3 ± 6.7	0.26
26	449-061C	*Macoma calcarea*	74.0 ± 6.3	0.37
27	449-061D	*M. truncata*	70.1 ± 5.9	0.53

Table 4
Comparing results between different dating methods applied to different materials taken from the same stratigraphic level of an archaeological cave-site.

Sampling location	ESR age (ka) (land snails)[a]	ESR age (ka) (tooth enamel)[b]	Biostratigraphic age (spores and pollen)[c]
A Lower Palaeolithic cave-site in the Northern Caucasus (Treugol'naya Cave)	393.0 ± 27.0	406.0 ± 14.9	MIS 11 (interglacial optimum)

[a] Molodkov, 1996a, 2001.
[b] Blackwell et al., 2005.
[c] Levkovskaya, 2007.

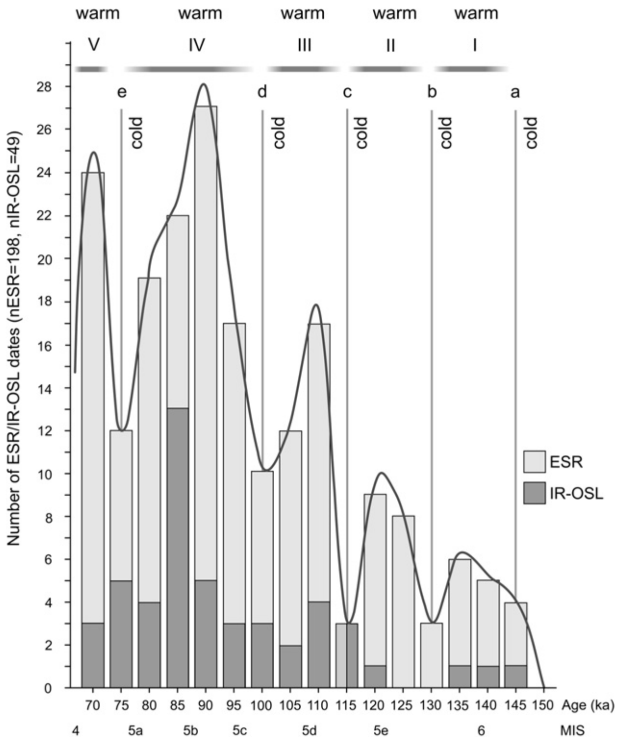

Fig. 3. Frequency distribution of mollusc-based ESR ages of transgressive marine sediments and feldspar-based IR-OSL ages of inter-till palynologically characterized terrestrial deposits from the climate-sensitive regions of Northern Eurasia between 145 and 70 ka (updated from Molodkov and Bolikhovskaya, 2009). Periods of relatively warm and cool climate are indicated according to palaeoclimatic reconstructions and U–Th chronology of speleothems from the northern Norway caves (after Lauritzen, 1995).

It is worth noting here that three shells (RLQG 418-, 421- and 422-090A), of those 5 presented in the table, are highly sensitive to open system behaviour, i.e. unpredictable uptake or loss of U from the shells during their burial. This is because of relatively low U, Th and K contents in the enclosing sediments. Therefore, the major contribution to the total dose rate is due to internal radiation of the shells (~65% in RLQG 418-090, ~80% in 421- and ~40% in 422-090A). In such cases, and also if the shell clearly behaves as an open system for U (e.g. RLQG 422-090A), precise determination of time-averaged U content in the shells becomes highly critical.

Table 3 shows some comparable results, obtained on parallel ESR dating of shells belonging to different species of molluscs. Some of the shells were taken from the same sampling point or enclosing sediment sample. Those marked with asterisk (*) are collected from the same sedimentary horizon at different depths and are shown in the table in stratigraphic order. A comparison of the results show a good conformity of the ages within each group of the shells collected from a particular sampling point(s), with any differences being within the error limits of the method. Of special interest are the latest results obtained on the shell samples collected from the lower Yenisei River area (RLQG 449-061A–D). The results demonstrate, once again, that even within the same environment different shells may behave differently: in the shell RLQG 449-061A the uptake of relatively large amounts of uranium (3.85 ppm) occurred soon after burial, whereas, in the other three shells uranium was accumulated in much lower (about one order of magnitude) concentrations. Taken as a whole, the data from the table demonstrate the potential of the method for precise and accurate ESR dating of the different shell species, both of marine and terrestrial (e.g. land snails) origin.

The comparative data for the oldest samples were obtained from a Lower Palaeolithic cave-site in the Northern Caucasus (Table 4). Shells of terrestrial pulmonate gastropod mollusc (land snail) *Monacha caucasicala* (Lindh.) and teeth were, independently and in different years, collected to determine absolute age for the culture-bearing layer of the cave deposits. Shells were dated to 393 ± 27 ka (Molodkov, 1996a, 2001) and teeth to 406 ± 15 ka (Blackwell et al., 2005). Palynologically, the dated layer was deposited during a very warm interglacial optimum, which, according to ESR dates, occurred in the second half of MIS 11. The first is from the bottom culture-bearing layer 7a of the cave and is dated to 583.3 ± 24.8 ka. The age of the layer has been determined on six shell samples of two land-snail species — *M. caucasicala* (Lindh.) and *Chondrula tridens* (Müll.) (see Table 3) taken from three different samples of enclosing sediments, indicated in the table by Roman numerals I, II and III.

An intercomparison for the youngest samples was performed on *Cerastoderma glaucum* shells. The sample has been ESR dated to 6310 ± 720 a, that corresponds to about 5540 conventional non-corrected radiocarbon a BP (calculated with CalPal software by Weninger et al., 2007). The parallel dating of the same shell samples by conventional ^{14}C and AMC ^{14}C techniques yielded the mutually consistent ages of 5474 ± 45 (Tln-2060) and 5515 ± 85 (Ua-10906) a BP obtained in Tallinn and Uppsala laboratories, respectively (Molodkov, 1996b).

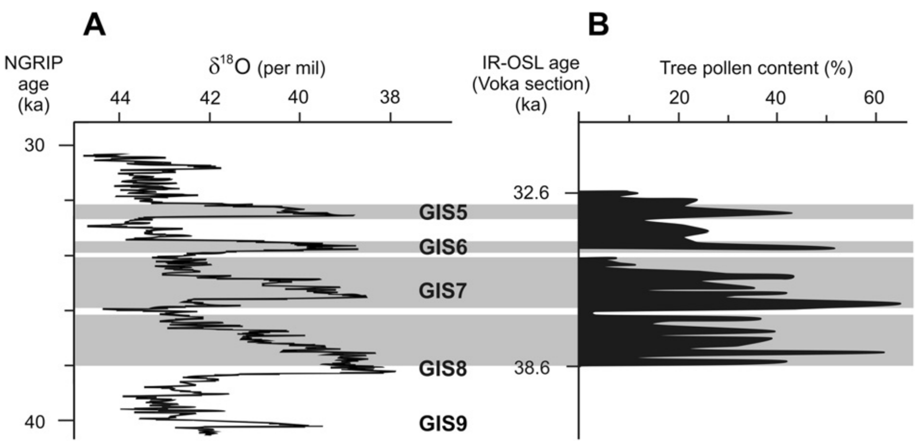

Fig. 4. Matching Voka chronoclimatic pattern (B) (after Bolikhovskaya and Molodkov, 2007) to $\delta^{18}O$ variations in NGRIP ice-core (A) (after Andersen et al., 2006). The best fit lies between Greenland interstadial (GIS) 8 and 5.

A good example of how mollusc-based ESR palaeoclimatic signals recorded over the last 900 ka correlate with those derived from terrestrial sequences is given in Fig. 2. Marine and terrestrial records shown in the figure were synthesized using our data, derived from different palaeogeographic provinces of Northern Eurasia (Molodkov and Bolikhovskaya, 2010). These data, reflecting climatic changes during the middle and late Pleistocene, were obtained from two independent sources: from palynological studies of reference sections in the glacial, periglacial and extraglacial zones and from mollusc-based ESR chronology of deposits, mainly of Eurasian Arctic marine palaeo-shelf origin, associated with warm climate intervals and marine transgressions. Clusters of ESR dates in the distribution of ages of mollusc shells, collected from palaeo-shelf sediments, revealed a series of intervals, correlative with marine transgressions. Intervals lacking ESR dates (ESR dating hiatuses) may be, in turn, interpreted as indicating relatively cold climatic conditions or the onset of glaciations in the Northern Hemisphere, accompanied by sea regressions, climate deterioration, and changes in the environments on the continent. As a rule, our ESR studies were accompanied by malacological analysis, the results of which are a good indicator of palaeoenvironmental conditions of the formation of fauna-bearing deposits. In some cases, valuable data were also provided by feldspar-based IR-OSL chronology of deposits from various parts of the palynologically characterized sedimentary sequences. This example demonstrates a good agreement between long pollen records and ESR/IR-OSL dated warm climate-related deposits for, at least, the last 600,000 years.

Another example of surprisingly good coincidence between ESR/IR-OSL palaeoclimatic records derived between 145 and 70 ka, mainly on marine palaeo-shelf deposits along the climate-sensitive arctic and subarctic regions of Northern Eurasia (Molodkov and Bolikhovskaya, 2009) and those obtained by stable isotope and U–Th analyses of speleothems from north Norwegian caves (Lauritzen, 1995) are shown in Fig. 3. The time-dependent frequency distribution of all the ESR and IR-OSL dates (ca 245) demonstrates the presence of high-frequency intervals (peaks I–V, Fig. 3) at ca 135, 120, 110, 90, and 70 ka, which may be correlated with periods of a relatively warm climate and flooding of the Arctic coastal areas. Low-frequency intervals (troughs b–e, Fig. 3) at ca 130, 115, 100 and 75 ka may be correlated with coolings and phases of sea regression. Our findings concerning the frequency distribution of ESR/IR-OSL dates for Northern Eurasia are in good agreement with the results from north Norwegian caves: according to high-resolution palaeotemperature proxy records and U–Th dating of the cave speleothems, periods of cooling were recorded in the coastal zone of northern Norway at ca 145, 139, 129, 114, and 100 ka. Although the cold interval at 75 ka has not been revealed in these caves, its isotope temperature signal is clearly visible in speleothems from caves in northwestern Romania (Lauritzen and Onac, 1999).

Also noteworthy, is an example of a temporal and environmental comparison of a high-resolution pollen and IR-OSL record of palaeoenvironmental changes between ca 39 ka to ca 33 ka BP derived from the Voka key section, located on the south-eastern coast of the Gulf of Finland (Bolikhovskaya and Molodkov, 2007), with $\delta^{18}O$ variations in the NGRIP ice-core (Andersen et al., 2006). This cross-record comparison shows a remarkable concordance of the palaeoclimatic signals recorded in both sites within the same time interval (Fig. 4). The best fit lies between Greenland interstadials (GIS) 8 and 5.

Table 5
Comparing results between ESR and two ^{14}C conventional age determinations obtained on the same *Cerastoderma glaucum* shell sample[a]. Sampling location: Hiiuma Island, north-western Estonia.

Method	Sample no.	ESR age (a)	ESR age converted into conventional ^{14}C age (a)	^{14}C age (a) (Tln-2060)	^{14}C age (a) (Ua-10906)
ESR	RLQG 210-094	6310 ± 720	5536 ± 647		
^{14}C	Tln-2060 (Tallinn)			5474 ± 45	
^{14}C	Ua-10906 (Uppsala)				5515 ± 85

[a] Molodkov, 1996b.

5. Conclusion

Comparison and cross-checking between different dating methods, both absolute and relative, were carried out in order to estimate the reliability of the dates obtained. The results of the study may be summarized as follows.

- Comparative results obtained on the same samples using different dating methods (ESR/IR-OSL/OSA, ESR-CS/ESR-OS/U–Th and ESR/^{14}C) on different types of sample materials (K-feldspars, quartz and biogenic carbonate) are in good agreement (Tables 1–4).
- The close correspondence of the palynological signatures of terrestrial sedimentary sequences and chronological successions of directly ESR- and IR-OSL-dated warm climate-related deposits over the last 900 and 310 ka, respectively, indicates that these completely independent records correlate fairly well (Fig. 2).
- High- and low-frequency intervals of the time-dependent frequency distribution of all the ESR and IR-OSL dates obtained within MIS 5 on transgressive marine and inter-till palynologically characterized terrestrial sediments from the climate-sensitive regions of Northern Eurasia are in good agreement with the results of oxygen isotope palaeoclimatic reconstruction and U–Th chronology of speleothems from the northern Norway caves (Fig. 3).
- Comparison of high-resolution IR-OSL- and pollen-based chronoclimatic succession recorded between 39 and 33 ka in the Voka section on the south-eastern coast of the Gulf of Finland with $\delta^{18}O$ variations in the NGRIP ice-core within the same time interval shows a remarkable concordance of the successions of palaeoclimatic signals in both records (Fig. 4).
- ESR ages obtained on land snails (393 ± 27 ka, Molodkov, 1996a, 2001) and tooth enamel (406 ± 15 ka, Blackwell et al., 2005) from a Lower Palaeolithic cave-site in the Northern Caucasus are in good agreement (Table 5). Palynologically, the dated layer was deposited during very warm interglacial optimum, which occurred in the second half of MIS 11, according to ESR dates.
- Good coincidence of the IR-OSL, OSA and ESR dating results obtained on K-feldspar and quartz grains and mollusc shells taken from the same enclosing sediments indicates no evidence of noticeable athermal emptying (anomalous fading) of the feldspar dosimetric traps even over the geological time scale.
- The results obtained in this study exemplify the potential of both combined and independent use of palaeodosimetric dating methods applied to two different minerals — feldspar and biogenic carbonate — to chronologically organize the sequence of the middle and late Pleistocene palaeoenvironmental events.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.quageo.2012.02.005.

References

Andersen, K.K., Svensson, A., Johnsen, S.J., Rasmussen, S.O., Bigler, M., Röthlisberger, R., Ruth, U., Siggaard-Andersen, M.-L., Steffensen, J.P., Dahl-Jensen, D., Vinther, B.M., Clausen, H.B., 2006. The Greenland ice core chronology 2005, 15–42 ka. Part 1: constructing the time scale. Quaternary Science Reviews 25, 3246–3257.

Bassinot, F.C., Labeyrie, L.D., Vincent, E., Quidelleur, X., Shackleton, N.J., Lancelot, Y., 1994. The astronomical theory of climate and the age of the Brunhes–Matuyama magnetic reversal. Earth and Planetary Science Letters 126, 91–108.

Blackwell, B.A., Liang, S., Golovanova, L.V., Doronichev, V.B., Skinner, A.R., Blickstein, J.I., 2005. ESR at Treugol'naya Cave, Northern Caucasus Mt., Russia: dating Russia's oldest archaeological site and paleoclimatic change in Oxygen Isotope Stage 11. Applied Radiation and Isotopes 62, 237–245.

Bolikhovskaya, N.S., 1995. The Evolution of Loess-Paleosol Formation of Northern Eurasia. Moscow University Press, Moscow (in Russian).

Bolikhovskaya, N.S., 2004. Paleoenvironments and Climatostratigraphy of the Loess-paleosol Formation of Northern Eurasia. LOESS in FORM 4. Geographical Research Institute of HAS, Budapest, pp. 11–36.

Bolikhovskaya, N., Molodkov, A., 2007. Pollen and IR-OSL Evidences for Palaeoenvironmental Changes between ca 39 kyr to ca 33 kyr BP Recorded in the Voka Key Section, NE Estonia, vol. 46. Geological Survey of Finland. Special Paper, 103–112.

Doğan, U., Koçyiğit, A., Varol, B., Özer, İ., Molodkov, A., Zöhra, E. 2012. MIS 5a and MIS 3 relatively high sea-level stands on the Hatay-Samandağı coast, Eastern Mediterranean, Turkey. Quaternary International, (in press).

Doronichev, V.B., Golovanova, L.V., Baryshnikov, G.F., Blackwell, B.A.B., Garutt, N.V., Levkovskaya, G.M., Molodkov, A.N., Nesmeyanov, S.A., Pospelova, G.A., Hoffecker, J.F., 2007. Treugol'naya Cave. The Early Palaeolithic in Caucasus and Eastern Europe. St. Petersburg (in Russian, with English summary).

Gusev E.A., Molodkov A.N., 2012. Structure of deposits formed during the final stage of the Kazantsevo transgression (MIS 5a) in the north of Western Siberia. Doklady Earth Sciences, 443(2), (in press).

Jaek, I., Molodkov, A., Vasilchenko, V., 2007a. Luminescent manifestation of tunnel and ionic processes in alkali feldspars. Journal of Applied Spectroscopy 74, 357–363.

Jaek, I., Molodkov, A., Vasilchenko, V., 2007b. On the possible reasons of anomalous fading in alkaline feldspars used for luminescence dating of Quaternary deposits. Estonian Journal of Earth Sciences 56 (3), 167–178.

Jaek, I., Molodkov, A., Vasilchenko, V., 2008. Instability of luminescence responses in feldspar- and quartz-based palaeodosimeters. Journal of Applied Spectroscopy 75, 820–825.

Jaek, I., Molodkov, A., Vasilchenko, V., 2010. The mechanisms of luminescence response to optical and thermal stimulation of alkali feldspars. Journal of Applied Spectroscopy 77, 441–444.

Jaek, I., Vasilchenko, V., Smirnov, J., 2003. Optically activated luminescence in a natural quartz. Journal of Applied Spectroscopy 70 (6), 896–899.

Lauritzen, S.E., 1995. High-resolution paleotemperature proxy record for the last interglaciation based on Norwegian speleothems. Quaternary Research 43, 133–146.

Lauritzen, S.E., Onac, B.P., 1999. Isotopic stratigraphy of a last interglacial stalagmite from northwestern Romania: correlation with the deep-sea record and northern-latitude speleothem. Journal of Cave and Karst Studies 61, 22–30.

Levkovskaya, G.M., 2007. Palinological data (Chapter 7). In: Golovanova, L.V., Doronichev, V.B. (Eds.), Treugol'naya Cave. The Early Palaeolithic in Caucasus and Eastern Europe. Saint-Petersburg, pp. 73–81 (in Russian, with English summary).

Molodkov, A., 1988. ESR dating of quaternary shells: recent advances. Quaternary Science Reviews 7, 477–484.

Molodkov, A., 1996a. ESR dating evidence on early man's dwelling at a Lower Palaeolithic cave-site in the Northern Caucasus. Geologija 19, 67–75.

Molodkov, A., 1996b. ESR dating of *Lymnaea baltica* and *Cerastoderma glaucum* from low Ancylus level and transgressive Litorina Sea deposits. Applied Radiation and Isotopes 47 (11/12), 1427–1432.

Molodkov, A., 2001. ESR dating evidence for early man at a Lower Palaeolithic cave-site in the Northern Caucasus as derived from terrestrial mollusc shells. Quaternary Science Reviews 20, 1051–1055.

Molodkov, A., Bitinas, A., 2006. Sedimentary record and luminescence chronology of the Lateglacial and Holocene aeolian sediments in Lithuania. Boreas 35 (2), 244–254.

Molodkov, A., Bolikhovskaya, N., 2009. Climate change dynamics in Northern Eurasia over the last 200 ka: evidence from mollusc-based ESR-chronostratigraphy and vegetation successions of the loess–palaeosol records. Quaternary International 201, 67–76.

Molodkov, A., Bolikhovskaya, N., 2010. Climato-chronostratigraphic framework of Pleistocene terrestrial and marine deposits of Northern Eurasia, based on pollen, electron spin resonance, and infrared optically stimulated luminescence analyses. Estonian Journal of Earth Sciences 59 (1), 49–62.

Molodkov, A., Dreimanis, A., Āboltiņš, O., Raukas, A., 1998. The ESR age of *Portlandia arctica* shells from glacial deposits of Central Latvia: an answer to a controversy on the age and genesis of their enclosing sediments. Quaternary Science Reviews 17, 1077–1094.

Molodkov, A., Bolikhovskaya, N., Miidel, A., Ploom, K., 2007a. The sedimentary sequence recovered from the Voka outcrops, North-Eastern Estonia: implications for late Pleistocene stratigraphy. Estonian Journal of Earth Sciences 56 (1), 47–62.

Molodkov, A., Jaek, I., Vasilchenko, V., 2007b. Anomalous fading of IR-stimulated luminescence from feldspar minerals: some results of the study. Geochronometria 26, 11–17.

Molodkov, A., Yevzerov, V., 2004. ESR/OSL ages of long-debated subtill fossil-bearing marine deposits from the southern Kola Peninsula: stratigraphic implications. Boreas 33, 123–131.

Vasilchenko, V., Molodkov, A., Jaek, I., 2005. Tunnel processes and anomalous fading in natural feldspars extracted from Quaternary deposits. Journal of Applied Spectroscopy 72 (2), 218–223.

Weninger, B., Jöris, O., Danzeglocke, U., 2007. CalPal-2007: Cologne Radiocarbon Calibration & Palaeoclimate Research Package. http://www.calpal.de/.

Zarhidze, D.V., Gusev, E.A., Anikina, N.Yu., Bartova, A.V., Gladenkov, A.Yu., Derevyanko, L.G., Krylov, A.V., Tverskaya, L.A., 2010. New data on stratigraphy of Pliocene-Quaternary deposits in the More-Yu River Basin (Bolshezemel'skaya tundra). Geological-geophysical Features of the Lithosphere of the Arctic Region 210 (7), 96–110 (in Russian with English summary).

Zarrina, E.P., 1991. Quaternary Deposits of the Northwestern and Central Areas of the Eastern Part of the USSR. Nedra, Leningrad (in Russian).