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ESR Dating of *Lymnaea baltica* and *Cerastoderma glaucum* from Low Ancylus Level and Transgressive Litorina Sea Deposits

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Freshwater gastropod (*Lymnaea baltica*) and brackish-water bivalve (*Cerastoderma glaucum*) shell samples from Ancylus Lake and Litorina Sea deposits on Hiiumaa Island (north-west Estonia) were subjected to ESR measurements. All *L. baltica* shells studied were composed of calcite and displayed typical multicomponent ESR spectra. *C. glaucum* shells normally show ESR spectra typical of aragonite with five radiation-induced lines. In the present work a *C. glaucum* with calcite-like spectra was encountered for the first time. The problem connected with accumulated palaeodose determination in shell fossils with unusual ESR spectra is highlighted. Copyright © 1996 Elsevier Science Ltd

Introduction

In a tectonically rising area of the Island of Hiiumaa (north-west Estonia), a typical Ancylus Lake mollusc fauna was for the first time found beneath the brackish-water Litorina Sea mollusc fauna, indicating the rapid regression of the lake at the end of the Ancylus stage as a consequence of the opening of a new outflow channel in the south-west of the Baltic. The drop in the water level has been estimated to be 20–25 m (Kessel and Raukas, 1967). The first attempt of Königsson and Olsson (1981) to date shells from low-lying Ancylus bearing layers on the islands of Öland and Gotland gave radiocarbon ages greater than 10,000 BP (the Younger Dryas period), in conflict with pollen analysis indicating that the layers belong to the early part of the Ancylus transgression (about 9600 BP, Svensson, 1994). Subsequent age determination on the same and some new sites by the AMS ^{14}C technique (Königsson and Possnert, 1988), using the inner fraction of the *Lymnaea peregra* f. *ovata* (= *Lymnaea baltica*) shells, showed a wide variation in ages from 11,260 to 8385 ^{14}C years BP. The last attempt to date the same sediments by optically stimulated luminescence (OSL) techniques (Königsson *et al.*, 1995) gave dates ca. 7000 BP that seemed too early. To establish the speed, time and amplitude of the regression more precisely, a new attempt to evaluate the age of the freshwater deposits characterizing the lowest position of the Ancylus Lake water level, and overlying Litorina sands in the Partsi section (Hiiumaa Island) was recently undertaken (Raukas *et al.*, 1996a). In the present work attention is focused on the ESR-dating of a fresh water Gastropod (*Lymnaea baltica*) and brackish-water Pelecypod *Cerastoderma glaucum* species. The studies showed that all *L. baltica* shells were composed of calcite, and displayed typical ESR spectra with a characteristic hyperfine sextet and the forbidden transition associated with the Mn^{2+} in shell carbonate. The phase sensitivity detection (PSD) technique was used to enhance the analytical line at $g = 2.0012$, $\Delta Bpp \approx 0.22$ mT and to suppress the manganese signals as well as the interfering radiation-induced signals in the region of $g = 2.00$. In contrast to *L. baltica* shells, molluscs from the *Cardiidae* family, as is generally known, always have shells of aragonite. In the present work about 10% of the aragonite in one *C. glaucum* shell sample had been diagenetically altered to calcite, a modification that could be expected to result in a slight underestimation of the age due to loss of accumulated palaeodosimetric information. The sample showed a calcite-like ESR spectrum. Furthermore, in the ESR spectra of *C. glaucum* signals were observed that are not normally recorded in the spectra of calcite shells. The use of high microwave power (HMP), overmodulation (OM) and phase sensitivity detection (PSD) techniques to separate analytical line at $g = 2.0012$ failed due to strong interference of the signal with an unusual signal at $g = 1.9975$, $\Delta Bpp \approx 0.32$ mT. The main aim of the present paper is to report efforts to eliminate the effect of interfering signals, and to estimate the age of low-lying Ancylus Lake and subsequent Litorina Sea deposits using the ESR dating of embedded shell fossils.

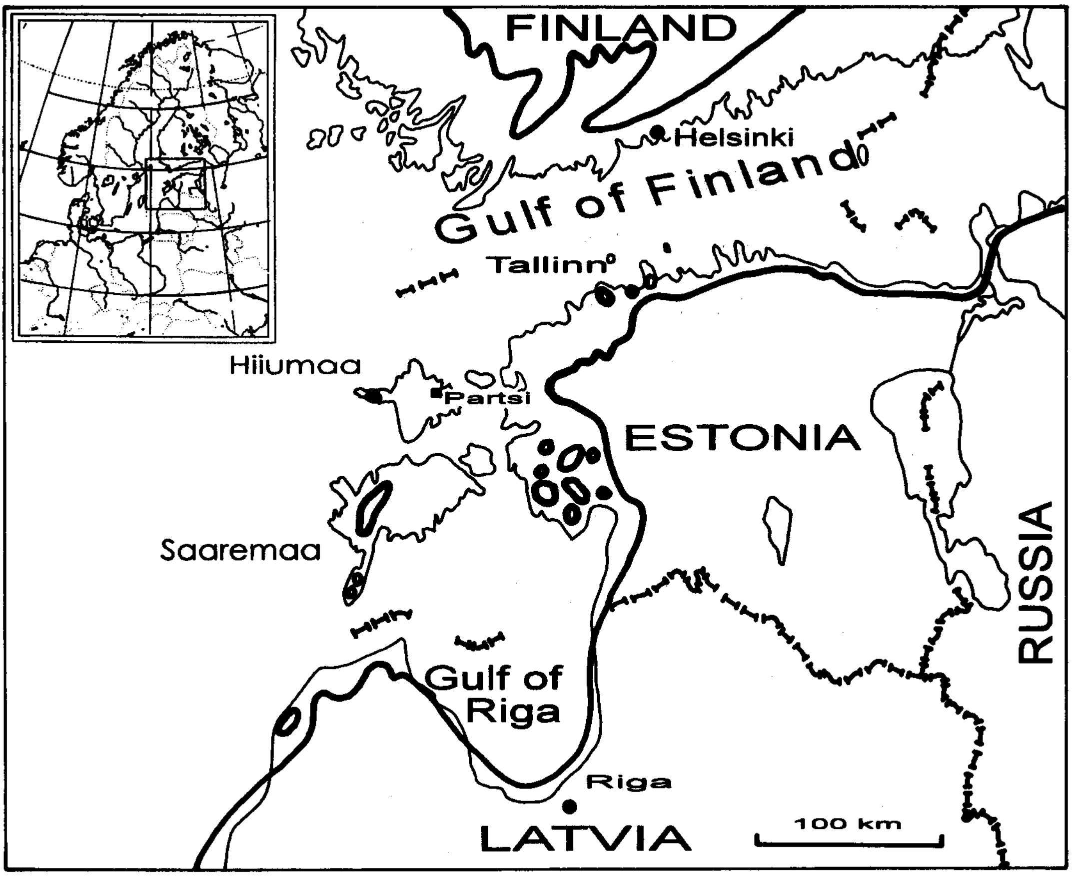

Fig. 1. Map of the study area showing Ancylus transgression shoreline.

Geological Setting

Shell samples were taken near the Partsi settlement on the Island of Hiiumaa, Estonia (Fig. 1). The quarry at Partsi exposes a long section of inclined bedded sandy gravels, shingles and cobbles. This coarse-grained bed and underlying sands at an absolute height of 10–15 m contain freshwater molluscs. Covering sands in the uppermost part of the section at an absolute height of about 18 m contain brackish-water molluscs. The thickness of the Ancylus and Litorina sediments is 7–8 m (Raukas *et al.*, 1996a). According to Raukas *et al.* (1996a), the 163 shells found in the medium-grained sand in the lowermost part of Ancylus sediments at a height of about 12 m were dominated by *Lymnaea baltica*

Table 1. ESR results and radioactivity data for samples from Ancylus Lake and Litorina Sea deposits

Shell species	*Lymnaea baltica*				*Cerastoderma glaucum*			
Sample number	209-094				210-094			
Thickness (μm)	100				350			
Removed (μm)	20				20			
U_{int} (ppm)	0.2				0.2			
D_{int} (μGy a^{-1})	23				24			
$\tau_{2.0012}$ (Ma)	1.14				1.14			
Palaeodose (Gy)	9.06				6.12			
Sediment sample number	111	112	113	114	107	108	109	110
Sediment type	Sand				Sand with shingles			
Fraction	Sand	Sand	Sand	Sand	Sand	As found	Shingles	Sand
U (ppm)	0.18	0.25	0.28	0.50	0.61	0.33	0.18	0.32
Th (ppm)	1.58	1.22	1.56	1.03	2.16	2.21	1.30	2.13
K (%)	0.78	0.73	0.77	0.74	0.76	0.59	0.57	0.78
$D_{\gamma ext}$ (μGy a^{-1})	291	269	300	288	364 (295)	295	—	337 (295)
$D_{\beta ext}$ (μGy a^{-1})	612	578	620	608	509	392	—	495
D_c (μGy a^{-1})	114				153			
D_Σ (μGy a^{-1})	1040	983	1056	1033	980	860	—	968
ESR age (a)	8750	9250	8610	8820	6250	—	—	6360
Mean (a)	8860 ± 700				6310 ± 720			

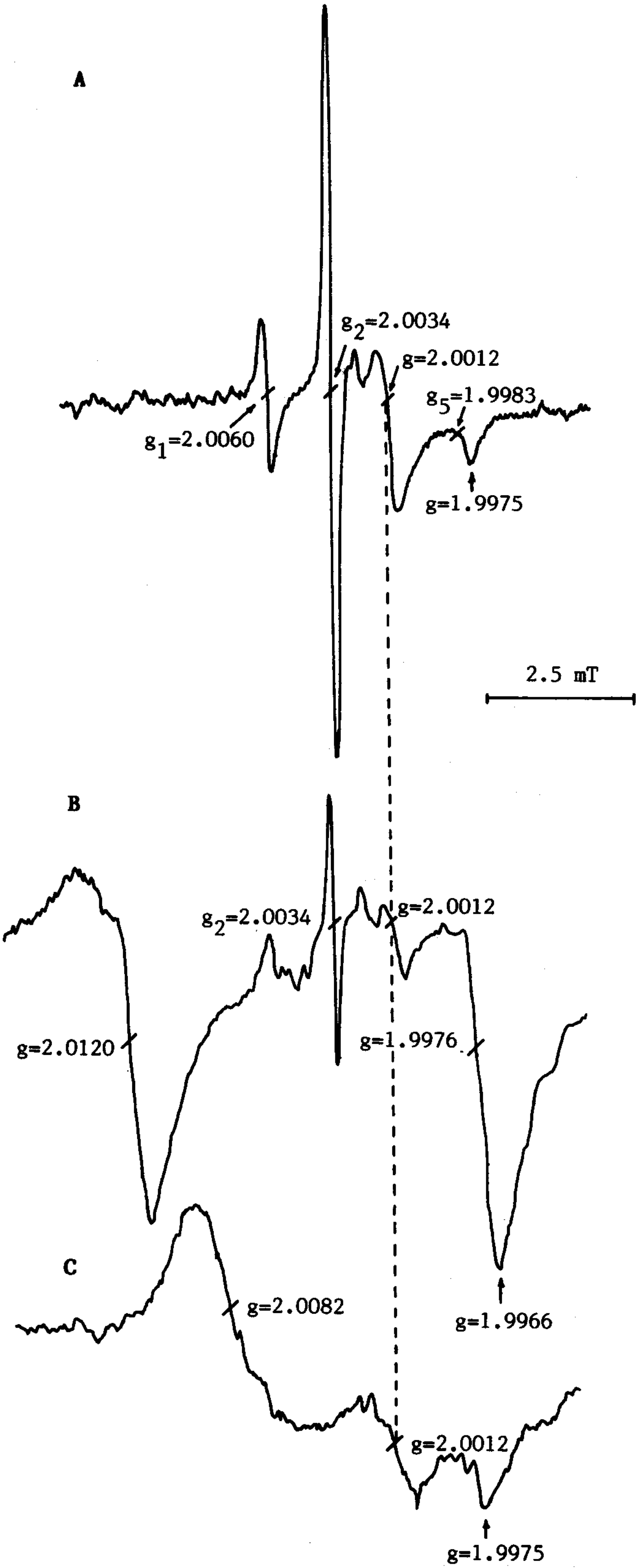

Fig. . Typical ESR derivative absorption spectrum of aragonite *Cerastoderma glaucum* mollusc shells (A) and the central part of the spectrum of the same shell species encountered in the present study (B); the expansion of the central part of the typical *Lymnaea baltica* shell sample spectrum between the third and fourth lines of Mn^{+} is also shown (C). The spectra were recorded at a microwave power of mW and modulation amplitude of . mT.

(60.7%) and *Bithynia tentaculata* L. (18.4%). Accompanying these were *Ancylus fluviatilis* (5.5%) and other typical Ancylus Lake species. Of 176 typical brackish-water molluscs found in the overlying Litorina sands at a height of about 18 m, *Cerastoderma glaucum* made up 78.6% and *Macoma baltica* 13.6%. Our investigation of the Partsi section in Hiiumaa demonstrates that the low-lying Ancylus fauna here belongs *in situ* to the very end of Ancylus time or to the subsequent transitional Mastogloia (Clypeus) stage. Both the Ancylus and the following Litorina mollusc fauna mostly occurred in a near-shore environment, several meters below water surface. With a view to simplifying dosimetric calculations, collected samples included only shells that were surrounded by sand to a distance of at least 8 mm.

Experimental

Sample preparation

For ESR analysis the shell samples were washed in water; the remnant sand and clay minerals were removed in an ultrasonic bath. The shells were etched in 10% acetic acid for 5 min in order to remove the α-irradiated surface, and then ground in an agate mortar. The size fraction of 75–400 μm was used for ESR analysis. Each sample was divided into 11 aliquots, 400 mg each. Of those 10 were irradiated by a calibrated ^{60}Co gamma source (delivering 1.48×10^{-2} Gy s^{-1}) at doses ranging from 15 to 150 Gy with radiation steps of 15 Gy. After irradiation, all shell aliquots were annealed for 2.5 h at 100°C to reduce the effect of short-lived signals.

ESR analysis

Aliquots were analyzed at room temperature with an ERS-221 spectrometer (X-band) manufactured by the Akademie der Wissenschaft of the former DDR. All *L. baltica* shells (sample no. 209-094) were composed of calcite. Their ESR spectra were strongly affected by the mutual interference of radiation-induced lines with intense Mn^{2+} signals. To suppress the manganese signals, enhance the analytical line at $g = 2.0012$, $\Delta Bpp \approx 0.22$ mT and 'filter out' the adjacent radiation-induced signals at $g_2 = 2.0034$, $g_3 = 2.0022$ and $g_5 = 1.9983$, the phase sensitive detection (PSD) technique was used (Molodkov, 1988, 1993). ESR spectra of the *L. baltica* shell samples were recorded with a sweep width of 200 mT, a scan time of 1620 s in the region of $g = 2.00$, and time constant of 0.01 s. Reported results are the average of 10 measurements of the 2.0012 signal for each aliquot. To determine the accumulated palaeodose, P_s, a logarithmic transformation was made of dose vs ESR intensity. Saturation intensity was determined iteratively by optimizing the correlation coefficient r.

In contrast to *L. baltica* most of the radiation-induced lines observed in the ESR spectrum of *C. glaucum* shell sample (No. 210-094) are strongly affected by a wide signal at $g = 1.9976$, $\Delta Bpp \approx 0.32$ mT. This signal overlaps the lines at $g_2 = 2.0034$, $g_3 = 2.0022$ and $g_5 = 1.9983$ and the analytical line at $g = 2.0012$, hampering its use for dosimetric read-out. The particulars of ESR-analysis of *C. glaucum* shells will be discussed in the following section.

Dose-rate measurements

The external dose rate induced by matrix was calculated from the measured values of $^{238}U + ^{235}U$, ^{232}Th and ^{40}K using an 1024-channel gamma spectrometer with a 150 × 100 mm NaI:Tl scintillation detector. The overall uncertainty was less than 2–4%. Four samples of about 1 kg each were taken within the sphere with $R \approx 30$ cm for the assessment of the gamma and beta contribution to the external

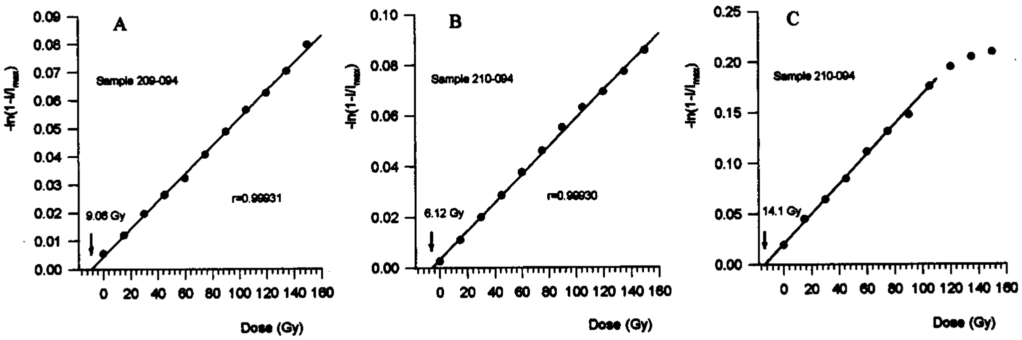

Fig. 3. Dose response curves of *Lymnaea baltica* (A) and *Cerastoderma glaucum* (B) shell samples. Each phase sensitive detection (PSD) measurement for the *L. baltica* sample was repeated up to 10 times for every dose and the mean taken. All measurements for *C. glaucum* samples (B) were normalized to A'_2 signal intensity (see Fig. 4). Dose dependence recorded by high microwave power (HMP) technique is also shown (C): due to interference of the signals at $g = 2.0012$ and $g = 1.9976$ turn-down of the curve has occurred at the higher doses. The palaeodose derived in (C) from the linear section of the dose response curve is overestimated about twice as much as obtained by the more realistic evaluation of the accumulated palaeodose in (B).

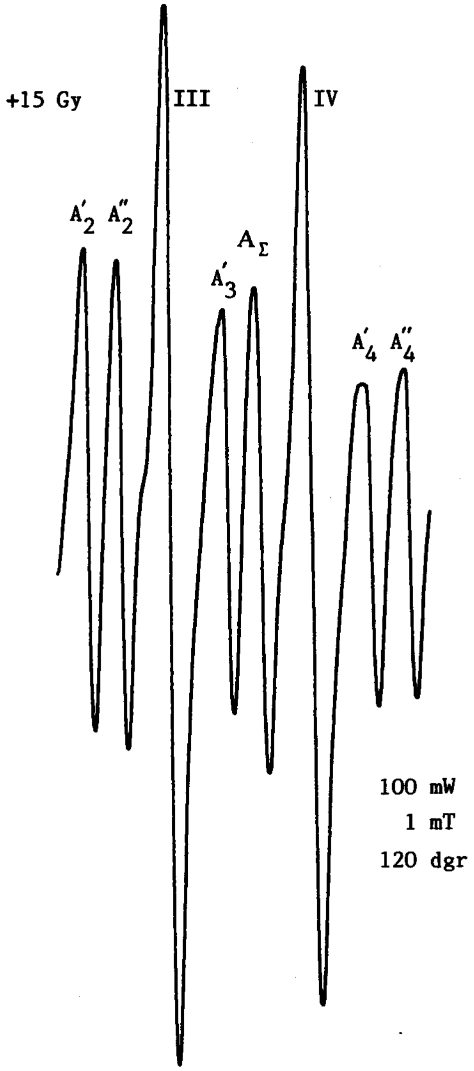

Fig. 4. The central part of the ESR spectrum of the *Cerastoderma glaucum* shell sample. The amplitude of the dating signal, $A_{2.0012}$, was determined by subtraction of the 'forbidden' signal, A''_3, from the sum signal $A_\Sigma = A_{2.0012} + A''_3$. The spectrum was recorded in phase sensitive detection mode of operation. Phase shift was normalized to 'forbidden' signal intensity, A'_2.

dose rate. The sedimentary beta dose rate was calculated from gamma ray spectra of the sand sample. Gamma dose component was derived from analysis of the samples with natural proportion of sand and shingles (6:4) (see Table 1). Estimates of the cosmic dose (Prescott and Stephan, 1982) were based at the half-depth of burial. The dose-rate conversion factors of Nambi and Aitken (1986) were used. The percentage of the beta dose was estimated according to the shell geometry and proportions etched off. The gamma-dose measurements were made on naturally damp sediment (water content: 15%). Internal dose rate was calculated basing on the determination of U-concentration in the shells by neutron activation analysis. The alpha-efficiency was assumed to be 0.15.

Results and Discussion

Table 1 summarizes the experimental results and the ESR ages. The date calculation for the sample has yielded an ESR age of 8860 ± 700 yr BP. The age obtained on freshwater deposits is consistent with the expected age of maximum Ancylus regression phase A_{VI} in the southern part of the Gulf of Finland [about 8000 years BP (Kessel and Raukas, 1967)].

Age determination of the *C. glaucum* shell sample encountered some difficulties. The radiation-induced (dating) signal is strongly affected by a signal which is characterized by g-factor of 1.9976 and linewidth of about 0.32 mT [Fig. 2(B)]. Microwave saturation experiments reveal that like the signal at $g = 2.0012$, $\Delta Bpp \approx 0.22$ mT, the 'forbidden' line at $g = 1.9976$ saturates far less than all other radiation induced signals g_1–g_5. The interference of the $g = 1.9976$ line with the $g = 2.0012$ signal results in a paleodose derived by the additive dose method that is more than twice the expected value [Fig. 3(C)]. As a rule, concentration measurements of the $g = 2.0012$ center in the shell carbonates can best be made by different combinations of unconventional techniques: over-modulation (OM), high microwave power (HMP), phase sensitive detection (PSD), etc. Efforts to eliminate signal interference by such techniques alone failed in this instance.

The following considerations, however, did allow a reasonable determination of the dose-response for this sample. The comparison of the central part of the ESR spectra of the samples irradiated with different artificial doses shows that 'forbidden' lines somewhat differ by amplitudes. The amplitude of the second line of each pair of 'forbidden' lines was normally 2–10% greater than that of the first line. Additionally, amplitude ratios A'_2/A''_2 and A'_4/A''_4 of the adjacent pairs of signals (see Fig. 4) normally differ by 2% in average. Thus it is possible to determine the amplitudes of the sum signal components A''_3 and $A_{2.0012}$ in ESR spectra of every recorded aliquot:

$$A''_3 = 2A'_3/(A'_2/A''_2 + A'_4/A''_4);\ A_{2.0012} = A_\Sigma - A''_3$$

All ESR spectra of the *C. glaucum* shell samples were recorded in the PSD mode of operation. The measured signal intensities were normalized in respect of A'_2 signal amplitude that helps to increase the reading precision and to reduce errors associated with uncertainty in adjustment of phase shift. The intensity of the corrected signal at $g = 2.0012$ is proportional to absorbed dose as determined by previous studies. Figure 3(B) shows the ESR results of dose response experiments plotting corrected and normalized signal intensity as a function of artificial gamma dose for irradiated *C. glaucum* shell samples.

The sample has been dated as 6310 ± 720 yr BP (Table 1) that corresponds to about 5500 conventional non-corrected radiocarbon yr BP (see e.g. Stuiver and Pearson, 1993). Recent datings of the same shell samples by conventional ^{14}C and AMC ^{14}C techniques yielded the similar ages of 5474 ± 45 (Tln-2060) and 5515 ± 85 (Ua-10906) yr BP, respectively (Raukas *et al.*, 1996b). The mutually consistent results obtained by different methods imply no underestimation in ESR age determination due to diagenesis as it has been previously assumed.

Conclusion

The ESR technique applied to the *Lymnaea baltica* and *Cerastoderma glaucum* mollusc shells from Ancylus Lake and Litorina Sea deposits has given reasonable ages within these two stages in the Baltic Sea history. The dating obtained for freshwater deposits is consistent with the expected age for the very end of the Ancylus regression. The dating on brackish-water deposits also agrees with the chronological data available on Litorina stage (7200–4200 conventional ^{14}C yr BP, Hyvärinen *et al.*, 1988). The present work shows also that the amplitude of the signal at $g = 2.0012$ can be determined in the ESR spectra of a *C. glaucum* mollusc shell sample even if it is superimposed by a very strong and wide signal of nonradiational origin. This work demonstrates that internally consistent age estimates may be obtained, even on geologically very young carbonate fossils with complex ESR spectra, that agree with independent geological evidence. The data obtained show that ESR is an appropriate tool for distinguishing several critical periods in the post-glacial Baltic Sea history and confirming ages of specific phases of ancient bodies of water.

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