

ESR DATING OF QUATERNARY SHELLS: RECENT ADVANCES

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This paper deals with the key problems of the ESR dating of subfossil mollusc shells — the estimation of the stored palaeodose of natural radiation. It is shown that the use of the analytical line (or peak in the integrated spectrum) at $g = 2.0012 \pm 0.0001$ with the half-width 0.6 mT seems most advisable for the estimation of the relative concentration of radiation defects equivalent to the stored palaeodose in the calcareous shell skeleton. Optimal ESR spectrometer settings have been determined. Results of ESR dating of subfossil mollusc shells from Eemian deposits of Boreal transgression are discussed.

INTRODUCTION

In recent years attention has turned toward electron spin resonance (ESR) as a new developing dating method. The foundation of the method lies in the effect of storage of radiation defects, equivalent to the palaeodose P , in geological objects which takes place under influence of natural radiation D from the environment. The age of the object, T , is determined by comparing the stored palaeodose, accumulated during geological time with the intensity of α - and β -particle fluxes as well as those of γ -quanta and cosmic radiation: $T = P/D$.

From the literature dealing with the elaboration of the new dating method (e.g. Grün and Schwarcz, 1987; Ikeya and Ohmura, 1984; Hennig and Grün, 1983; Molodkov, 1986; Radtke *et al.*, 1985; Skinner, 1985) it appears that difficulties lie both in the estimation of palaeodose and its accumulation rate (= annual dose). To a certain extent this is accounted for by differences in the nature of paramagnetic centres of different geological and archaeological objects, in the conditions of palaeodose accumulation, and also by complexity of ESR spectra interpretation.

This paper presents some results obtained recently in elaborating the ESR method for dating subfossil shells.

DETERMINATION OF PALAEODOSE

The ESR dating technique is usually based on the measurement of polycrystalline samples of different genesis and age. At the same time, the overwhelming majority of fundamental studies is carried out on artificially irradiated monocrystals, where, as a rule, the spectrum is unambiguously related to one or another defect. Besides, there occur considerable difficulties in precision measurement of even relative defects' concentration due to a great number of physical factors affecting the value of output signal of absorption at resonance. This makes the evaluation of palaeodose of natural radiation equivalent to natural

concentration of radiation defects in the geological object rather complicated.

There is also a remarkable uncertainty associated with the choice of the analytical line in the ESR spectrum for the study object. So, for example, the following radiation-induced ESR spectral lines were used for dating subfossil shells: $g = 2.0010$ (Tsuji *et al.*, 1985), $g = 2.0044$ (Ninagawa *et al.*, 1985), $g = 2.0008$ (Ikeya and Ohmura, 1984) and $g = 2.0020$ for dating of Holocene shells (Molodkov and Hütt, 1985).

As a measure of relative concentration of radiation defects, peak-to-peak height of corresponding lines has been used by the majority of investigators. For an analytical line Ikeya and Ohmura (1984) proposed to use half of the magnitude of the derivative line at $g = 2.0008$ whereas Radtke *et al.* (1985) used the amplitude from low field wing of the line at $g = 2.0023$ up to the lower peak of line at $g = 2.0007$ (Fig. 1a).

Attempts have also been made to use the area under the absorption curve as a palaeodose equivalent, the curve having been obtained by double integration of the first derivative spectra (Smith *et al.*, 1985, 1986; Yokoyama *et al.*, 1985); however, they did not prove successful.

Many investigators have pointed to the complex behaviour of the studied lines both on laboratory irradiation (Wieser *et al.*, 1985; Molodkov and Hütt, 1985) and on the thermal experiments (Yokoyama *et al.*, 1985), which considerably complicated the interpretation of differential ESR spectra. Palaeodoses, evaluated on the basis of different spectral lines for one and the same shell (and, hence, age) may differ up to 3–10 times (Molodkov and Hütt, 1985; Radtke *et al.*, 1985).

The results of dating of calcite shells proved especially contradictory; in their ESR spectra the radiation-induced signal is masked by intense lines of manganese isomorphous impurity Mn^{2+} . This is why some researchers (e.g. Radtke *et al.*, 1981) considered calcite shells less suitable for ESR dating.

These circumstances stimulated the author to pursue

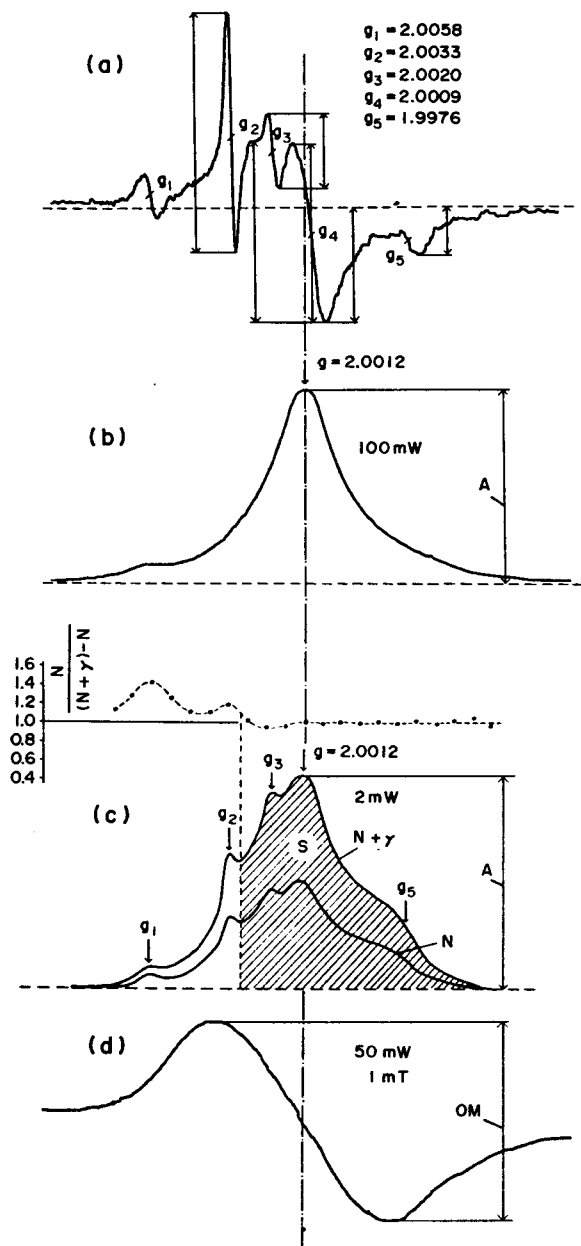


FIG. 1. Variations of concentration measurements in ESR spectra of mollusc shells: (a) on the lines of resolved differential ESR spectra: usage is hampered due to interference of lines; (b) on the amplitude (A) or on the area of the analytical peak at $g = 2.0012$; the use of higher microwave power allows the enhancement of this signal and the suppression of the adjacent peaks; (c) on the amplitude of the analytical peak at $g = 2.0012$ (A) in the resolved (at low microwave power) integrated ESR spectrum or on the area (S) in the region of the magnetic field with the good plateau; (d) on the peak-to-peak height of the analytical line at $g = 2.0012$ in differential spectrum (OM); the signal is easier to record and to use for reliable concentration measurements.

further detailed studies in this field, aimed at finding an alternative method for the estimation of the accumulated palaeodose in shells with different crystalline structures and ages.

For these purposes, integrated and differential ESR spectra of shells with natural and laboratory radiation doses were analysed. The spectra obtained during thermal experiments, and those recorded for different values of microwave power in cavity, were also studied.

As a result of these studies it was established that in the radiation-induced signal for both aragonite and calcite shells the absorption signal with $g = 2.0012 \pm 0.0001$ and a half-width of about 0.6 mT (Fig. 1b) dominates, presumably belonging to the radical CO_3^{3-} (Serway and Marshall, 1967; Marshall *et al.*, 1968). Previously, a line with the same g -value was described by Radtke *et al.* (1985) for synthetic aragonite.

This signal is not detected in the resolved differential ESR spectrum of shells, because from the side of low field it interferes with the line at $g_3 = 2.0020$, and from the side of high field with the line at $g_5 = 1.9976$; the latter most probably belongs to defects of CO_2^- type (DeCanniere *et al.*, 1985). In this spectrum the line at $g = 2.0012$ is detected as a part of its high field wing with g -value at $g_4 = 2.0009$. Thus, determination of relative defect concentrations is rather complicated on the basis of superimposed lines in the ESR spectrum. Therefore the amplitudes of the lines in the derivative absorption spectrum will be determined not only by relative concentration of different defects, but also by differences in their parameters (spin-lattice relaxation times, life-times etc.), as well as by the conditions of the ESR spectrum registration which may bring about serious mistakes in determining the palaeodose, the age of the object and stability of the analytical signals.

In view of the above and in consideration of the dominating component $g = 2.0012$ in the absorption resonance signal, the author suggests the following methods for the estimation of relative concentration of radiation defects in the shell's mineral part (Molodkov and Hütt, 1985; Molodkov, 1986): method S — on the area under the resonance absorption curve, obtained by double integration of the first derivative spectra of the ESR with the correction for baseline. Integration is performed only in the region of the magnetic field with the good plateau (Fig. 1c); method A — on the amplitude of the peak at $g = 2.0012$ of the resonance absorption signal in the integrated ESR spectrum; method OM — on the peak-to-peak height of the analytical line at $g = 2.0012$ in the differential ESR spectra, registered with strong (up to 1 mT) over-modulation (Fig. 1d).

It should be mentioned that the behaviour of dose-response curves for derivative lines under conditions of artificial or natural irradiation is difficult to predict because of the interference of various components of complex ESR spectra. In contrast to this, the dose-response curves obtained by methods S, A and OM, are well represented by the exponential equation of first order kinetics:

$$I = I_{\infty} (1 - e^{-\mu(\gamma+P)})$$

where I is the signal intensity for a gamma dose, γ , I_{∞} is the saturation intensity (usually at the γ -dose of about 5 kGy), μ is the sensitivity coefficient, and P is the palaeodose.

TABLE 1. Results obtained from palaeodose determination on the basis of different signals

Sample	Palaeodoses P_i (Gy) for different signals						Expected palaeodose P_e (Gy)	ESR age T (ka)	Geological age (ka)	Annual dose D_a (μ Gy)
	g_3 2.0020	g_4 2.0009	g_5 1.9976	OM S A		P (OM,S,A) (Gy)				
				2.0012						
10-12-4	1075	1075	790	1068	1078	1070	1072	550 ± 33	300-690	1950
14-12-4	80	80	80	80	81	80	80	65 ± 8	55-70	1240
15-12-4	62	72	56	72	71	72	72	56 ± 4	55-70	1280
18-12-4	194	420	176	270	280	280	280	105 ± 11	~100	2666
24-12-4	85	132	110	114	107	111	111	92 ± 6	~100	1200
25-12-4	53	83	113	123	114	114	117	92 ± 7	~100	1270
26-12-4	44	97	53	84	84	84	84	82 ± 6	~100	1024
29-12-4	84	85	93	90	85	86	87	90 ± 8	~100	963
31-12-4	66	72	128	123	116	125	120	120 ± 8	~100	996
32-12-4	111	125	55	108	103	99	103	109 ± 7	~100	949

Table 1 presents palaeodoses obtained using these different methods. Ages of shells were calculated from averaged values of palaeodoses, determined by methods S, A and OM.

The comparison of the data presented in Table 1 shows that in some cases palaeodoses estimated by different methods coincide and yield the expected ages, e.g. samples NN 10-, 14-12-4; but for most of the palaeodoses determined on the basis of lines at g_3 , g_4 and g_5 great discrepancies are revealed.

STABILITY OF THE ANALYTICAL SIGNAL

In the present work the thermal stability of the analytical signal was evaluated on the basis of annealing temperatures by extrapolating the thermal experiment data to the low temperature region.

The isothermal annealing experiments were carried out for a shell, *Astarte borealis*, with the stored palaeodose of natural radiation 1072 Gy. Different shell portions were thermostated at six comparatively low temperatures — from 180°C to 100°C. The time τ corresponds to a reduction of the initial concentration of radiation defects to 1/e. The concentration of defects was measured on the basis of the peak at $g = 2.0012$ in the integrated spectrum and on the basis of the analytical line at $g = 2.0012$ of the derivative absorption spectrum, and for comparison, on the basis of lines g_3 , g_4 and g_5 in the differential ESR spectrum (Fig. 2).

Treatment of experimental data obtained from isothermal annealing in coordinates $\log \tau$ vs $10^3/T$ (Fig. 3) showed that at the ambient temperatures of 0°C and +10°C the life-time of the analytical line at $g = 2.0012$ is about 3×10^6 and 3×10^5 years, respectively.

In this work, life-times of adjacent peaks in integrated spectra were not determined. But they may be

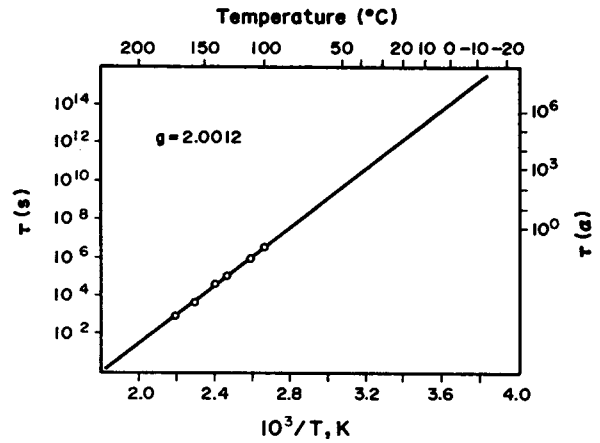


FIG. 3. Arrhenius plot of the signal at $g = 2.0012$ for the isothermal annealing experiment performed on shell with stored palaeodose of natural radiation 1072 Gy (sample N 10-12-4). The life-times at 0°C and +10°C are about 3×10^6 and 3×10^5 years, respectively.

supposed to have the same order of magnitude. The good plateau obtained by comparing integrated spectra of mid Pleistocene shells (Molodkov and Hütt, 1985) serves as good evidence for this as do the life-times obtained in the present work for the derivative lines g_3 , g_4 and g_5 ; e.g. at +5°C they are 1×10^6 , 0.56×10^6 and 0.2×10^6 years, respectively.

However, it should be borne in mind here that thermal annealing in the laboratory may differ from the process of natural relaxation of defects at ambient temperature during burial. Therefore, it is of importance to study the lower limit of the method by examining very ancient samples of up to several million years. This gives the opportunity to understand the natural process of the decay of defects within geological time intervals, and possibly estimate the beginning of thermodynamic equilibrium between decay and generation of radiation defects.

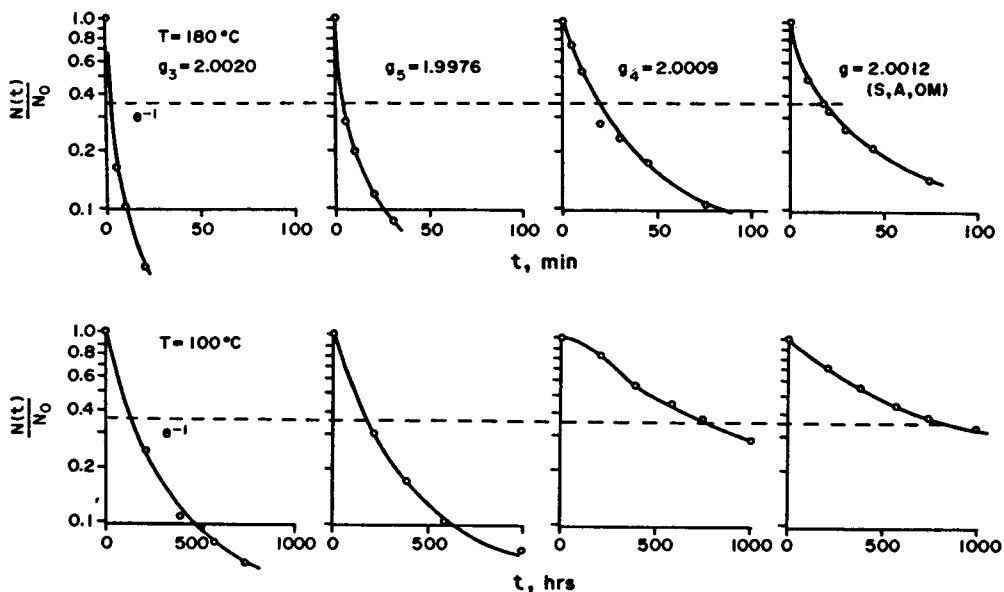


FIG. 2. Isothermal annealing of different signals at 180°C and 100°C. N_0 is the signal intensity before annealing, N_t — after time t .

PECULIARITIES IN DATING OF HOLOCENE SHELLS

On studying the potential for estimating the palaeodose of Holocene shells on the basis of an ESR spectrum with methods S and A, it appeared that the region of g -values characteristic for the signals of radiation defects in the integrated ESR spectrum of Holocene shells is overlapped by high field wing of wide signal (up to 2.5 mT) of non-radiation origin. Its intensity depends on several uncontrollable factors, such as duration and conditions of burial, degree and rate of the degradation of organic matter in the shell, its initial concentration, etc. As a result, correct estimation of the relative concentration of radiation defects in Holocene shells with the above named methods is complicated due to uncertainty in correlation of signals of different origin in the integrated resonance absorption spectrum.

Besides, Holocene shells are characterized by a quite low concentration of radiation defects which hampers their detection because of unsatisfactory 'signal-to-noise' ratio, interference with the lines of manganese, organic radicals, etc.

The problem related to the registration of the analytical line at $g = 2.0012$ was solved for Holocene aragonitic shells by using the effect of selective influence of microwave power in cavity on different components of the ESR spectrum. It was established

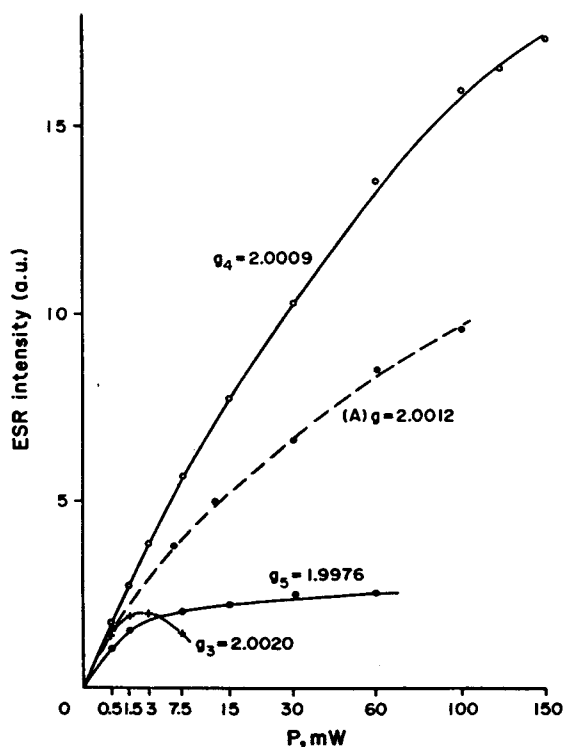


FIG. 4. Variation of the intensity of some ESR signals as a function of microwave power P in shell. Adjacent lines at $g = 2.0020$ and $g_5 = 1.9976$ are saturated at considerably lower microwave power than the line at $g = 2.0012$. The use of higher microwave power therefore enables the use of the latter as an analytical line for dating Holocene shells.

that the line at $g_3 = 2.0020$ reaches saturation at a microwave power of 2–3 mW, line at $g_5 = 1.9976$ at 5–10 mW, whereas the line at $g = 2.0012$ is not saturated even at a microwave power of 150 mW (Fig. 4).

Thus, as the adjacent lines g_3 and g_5 become saturated their effect on the analytical line at $g = 2.0012$ decreases in the differential ESR spectrum. At a microwave power of 80–150 mW the individual spectrum of this line is sufficiently distinct to use its peak-to-peak height as a measure of relative concentration of radiation defects (Fig. 5c).

In Holocene calcite shells, paramagnetic manganese is present as an impurity in such a concentration that its signal masks the signal of radiation damage used for dating (Fig. 5b). Here, the line at $g = 2.0012$ was separated in complex spectra of calcite shells by shifting the phase between high frequency modulation field and the reference signal of the synchronous detector (Griffiths *et al.*, 1983) by about 110 degrees. Due to differences in spin-lattice relaxation time of electron/hole centres in the shell crystalline lattice, it became possible with such a phase shift to suppress the hole-like signal of manganese in order to separate the analytical line at $g = 2.0012$ (Fig. 5d).

When dating Pleistocene shells, the separation of the analytical line at $g = 2.0012$ is considerably easier due to a more satisfactory ratio between the amplitude of the analytical line and the manganese lines.

Good results may also be obtained by subtracting the signal of forbidden manganese transition signal, which does not change under artificial irradiation, from the radiation-induced signal in the ESR integrated spectrum.

URANIUM UPTAKE

Several investigators (e.g. Ikeya and Ohmura, 1984; Radtke, 1986) have pointed out, and it follows from Table 2 as well, that at relatively low uranium concentrations in shells the internal component of the radiation dose contributes usually only 10–15% to the total palaeodose. Therefore it is most likely that the error of the internal dose cannot be the cause of blunders in dating of shells with such U-content.

However, it should be pointed out that the concentration of uranium in shell may be so high that the internal dose becomes comparable with the external one. Here, the uranium uptake model used is of decisive importance, otherwise the dating of shells with high uranium content (as well as the dating of bones; Grün and Schwarcz, 1987) becomes rather problematic.

In principle, when dating shells, as is the case with bones, one may use the models of early uranium uptake or of linear uranium uptake. The overwhelming majority of the shells studied in this work had a relatively low uranium concentration (0.2–2.5 ppm) and the correction of age did not prove difficult using the model of early uranium uptake.

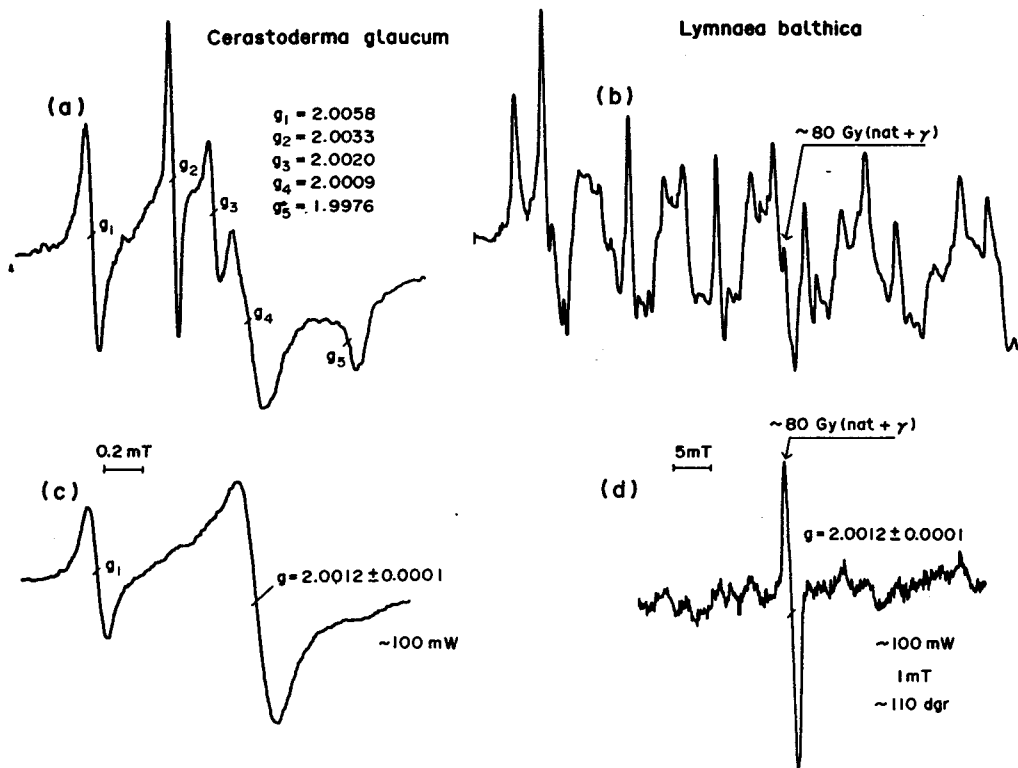


FIG. 5. Analytical line at $g = 2.0012$ (c,d), separated in the ESR spectrum of aragonite (a) and calcite (b) shells.

TABLE 2. Results of ESR dating of subfossil mollusc shells of an Eemian formation

Sample	Locality	Depth (m)	U (ppm)	Th (ppm)	K (%)	$D_{ext} \gamma, \beta + D_c$ ($\mu\text{Gy/year}$)	$\bar{D}_{int} \alpha, \beta$ ($\mu\text{Gy/year}$)	U_{in} (ppm)	P (Gy)	ESR age (ka)
24-12-4	Zaton	3.80-4.25	0.75	2.34	0.93	1072	130	0.70	110.6	92 ± 6
25-12-4	Zaton	4.25-4.65	0.55	2.05	1.09	1174	98	0.50	117.0	92 ± 7
26-12-4	Zaton	4.25-4.65	0.55	2.05	1.09	920	104	0.60	84.0	82 ± 6
27-12-4	Zaton	4.65-5.60	0.55	2.05	1.09	1130	28	0.20	110.0	95 ± 15
28-12-4	Zaton	4.65-5.60	0.55	2.05	1.09	1111	85	0.50	110.0	92 ± 9
29-12-4	Zaton	4.65-5.60	0.55	2.05	1.09	717	245	0.90	86.6	90 ± 8
30-12-4	Zaton	4.65-5.60	0.55	2.05	1.09	914	128	0.50	93.8	90 ± 8
31-12-4	Zaton	5.60-6.40	0.41	1.62	1.10	885	111	0.50	119.5	120 ± 8
32-12-4a	Zaton	5.60-6.40	0.41	1.62	1.10	835	114	0.50	103.4	109 ± 7
32-12-4b	Zaton	5.60-6.40	0.41	1.62	1.10	835	106	0.50	98.8	105 ± 7
34-04-7	Bychje	8.00-8.90	1.03	5.10	1.53	1790	1080	5.50	132.0	—
35-04-7	Bychje	8.00-8.90	1.03	5.10	1.53	1320	1590	8.30	125.3	—
36-04-7	Bychje	10.10-10.90	0.85	4.90	1.45	1170	120	0.55	105.6	82 ± 7
37-04-7	Bychje	10.10-10.90	0.85	4.90	1.45	1312	130	0.65	115.0	80 ± 8
38-04-7	Bychje	10.10-10.90	0.85	4.90	1.45	1300	230	0.95	132.0	86 ± 8
39-05-7	Bychje	10.10-10.90	0.85	4.90	1.45	1270	200	0.77	132.0	90 ± 8
40-05-7	Yelkino	12.10-13.20	0.63	2.52	0.91	760	80	0.40	68.6	82 ± 7
41-05-7	Yelkino	12.10-13.20	0.63	2.52	0.91	940	180	0.66	91.5	82 ± 11
42-05-7	Yelkino	12.10-13.20	0.63	2.52	0.91	830	140	0.57	81.6	84 ± 8

However, it recently turned out that in the collection there are also shells (NN 34- and 35-04-7) with anomalously high uranium content (5.50 and 8.30 ppm, respectively; Table 2). These, together with the remaining 17 samples were supposed to have been collected from coeval deposits (about 100 ka). The palaeodoses stored by all these shells as well as uranium concentrations of the embedding sediments reveal no remarkable differences. Therefore, we assume that in this case we have a different uranium uptake model, e.g. a sublinear one (so named by Grün and Schwarcz, 1987), i.e. most of the uranium was accumulated during

the latter period of burial. Possibly this U-uptake took place very late as it did not cause considerable growth in palaeodose.

It should be borne in mind that, in principle, in many cases uranium loss may occur as well as uranium uptake. Thus, it should be pointed out that the present-day U-content does not provide a reliable reflection of post-sedimental U-uptake history (Fig. 6).

In order to avoid serious mistakes in the estimation of the internal component of the palaeodose, it is noteworthy to consider the link ^{234}U - ^{230}Th in the uranium decay chain as a low-pass filter, smoothing the

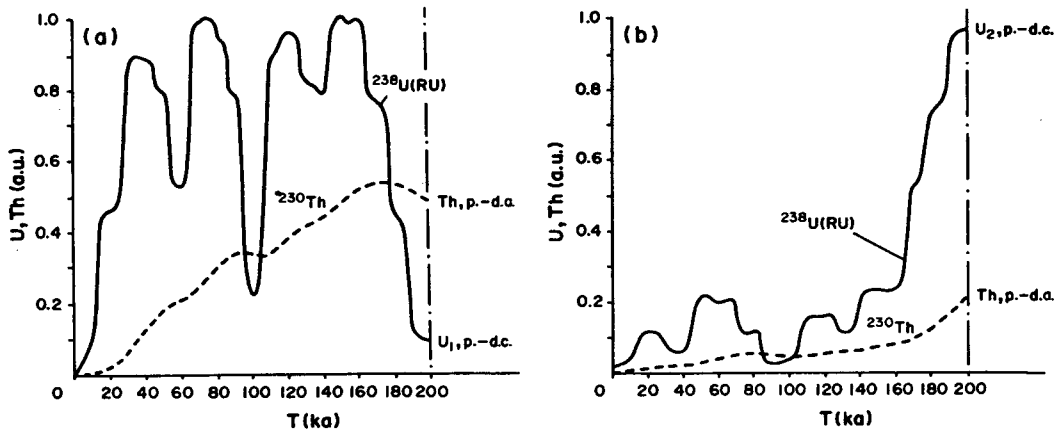


FIG. 6. Random U-uptake model. The use of present-day content (p.-d.c.) of uranium in shells for ESR dating may yield too old (a) or too young (b) ages; the use of present-day ²³⁰Th activity data for age correction allows the avoidance of blunders in age determination.

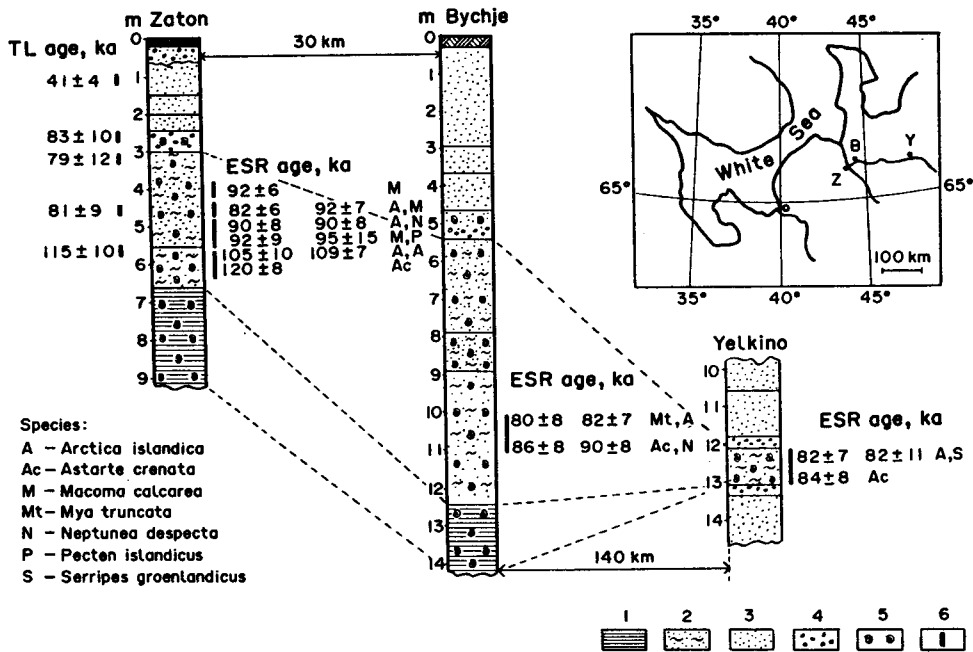


FIG. 7. Results of the ESR and TL dating of an Eemian formation in the Arkhangelsk District. 1 = clays; 2 = silty sand; 3 = sand; 4 = gravel and pebble; 5 = shells of molluscs; 6 = sampling depth.

potentially abrupt fluctuation of U-concentration in the shell during a considerably shorter period than the ²³⁰Th half-life (Fig. 6). That can be applied for the calculation of the averaged U-content on the basis of the data on present-day ²³⁰Th activity and apparent age $T = P/D_{ext}$, where D_{ext} is the external dose-rate. The succeeding age correction, in consideration of the averaged U-content, may be carried out according to the previously described technique (e.g. Molodkov, 1986).

DATING RESULTS

In order to evaluate the potential of the new and fast developing ESR dating method for solving some of the stratigraphical problems of the Northern part of the Soviet Union, three profiles from the basins of the

Mezen and Peza Rivers (Arkhangelsk District, about 100 km south of the polar circle) were selected as study profiles. These profiles of the Boreal transgression have been subjected to palynologic, micro- and macro-faunistic, mineralogical and granulometric studies since the end of the last century. The vast majority of investigators acknowledge the Eemian age of these deposits.

Shells of different mollusc species were selected for ESR dating; the shells were collected and presented by H. Putnik (Institute of Geology, Acad. Sci. E.S.S.R.). Later, these deposits were also dated by G. Hütt with the TL method using K-feldspars as palaeodosimeters.

The dates obtained within the time span 80 ± 8 and 120 ± 8 ka (Table 2, Fig. 7) are in good agreement with the modern estimates about the Eemian age of the deposits (Molodkov and Raukas, 1987) and also with

stage 5 of the marine chronological record (Shackleton and Opdyke, 1973). The shells from Zaton marine beds are probably Eemian also on the basis of aminostratigraphical investigations (Miller and Mangerud, 1986).

Unfortunately, at the time being I do not possess sufficient data on samples NN 34- and 35-04-7. Therefore, the dating of these shells is to be postponed for some time.

SUMMARY

The results of the present work may be summarized as follows:

- (1) The peak at $g = 2.0012 \pm 0.0001$ with the half-width 0.6 mT appears to dominate in the integrated spectrum of aragonite as well as calcite shells.
- (2) Isothermal annealing studies have revealed the lifetime of this peak to be about 3×10^6 and 3×10^5 years at temperatures of 0°C and +10°C, respectively.
- (3) The amplitudes of other peaks in the integrated spectrum of shells are, as a rule, insignificant. Lifetimes of the adjacent lines (at $g = 2.0020$ and $g = 1.9976$) seem to have the same order of magnitude.
- (4) The use of the analytical peak (line) at $g = 2.0012$ seems most advisable for the estimation of the palaeodose stored in shells.
- (5) The potential of estimating the inner dose in shell, in the case of the so-called random U-uptake, has been discussed.
- (6) Optimal ESR spectrometer settings have been determined.

The results of the dating can be summarized by the following points:

- (a) The radiation situation seems to have been rather stable with time at different burial sites.
- (b) Shells of different species, both aragonitic and calcitic may serve quite well as suitable ESR dating objects.
- (c) Variation of U-contents in shells, with rare exceptions, seems to be rather small in the region studied here.
- (d) The simultaneous dating of different shells from identical layers has turned out to be most advantageous.
- (e) On the basis of the good correlation obtained for the dates with the geological estimates and because of the correct age sequence with depth, it may be supposed that the ages obtained are quite reliable and the ESR technique may in fact be successfully used for determining the age of molluscs, which in turn sheds more light on the evolution of sea basins for example.

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